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(Nitroaromatics and Isophorone)

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EPA METHOD STUDY 19, METHOD 609

(NITROAROMATICS AND ISOPHORONE)

by

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The study design was based on Youden's plan for collaborative tests of analytical methods. Three Youden pair samples of the test compounds were spiked into six types of test waters and then analyzed. The test waters were distilled water, tap water, a surface water, and three different industrial wastewater effluents. The resulting data were statistically analyzed using the computer program entitled "Interlaboratory Method Validation Study" (IMVS). Mean recoveries of the subject compounds were in the range of 49-75 percent. Overall precision was in the range of 26-60 percent and single-analyst precision was in the range of 13-45 percent. In general, mean recoveries, overall standard deviations (S), and the single analyst standard deviations (SR) were directly proportional to the true concentration levels. There were no discernible differences due to water types among mean recovery, overall precision, and single-analyst precision.

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FOREWORD

Environmental measurements are required to determine the quality of ambient waters and the character of waste effluents. The Environmental Monitoring and Support Laboratory (EMSL)-Cincinnati conducts research to:

- Develop and evaluate techniques to measure the presence and concentration of physical, chemical, and radiological pollutants in water, wastewater, bottom sediments, and solid waste.
- Investigate methods for the concentration, recovery, and identification of viruses, bacteria, and other microorganisms in water.
- Determine the responses of aquatic organisms to water quality.
- Support an Agency-wide quality assurance program to assure standardization and quality control of systems for monitoring waste and wastewater.

This publication of EMSL-Cincinnati, entitled: EPA Method Study 19 Method 609 (Nitroaromatics and Isophorone) reports the results of EPA's Interlaboratory method study for the following priority pollutants:

Nitrobenzene (98-59-1)*	2,4-Dinitrotoluene (121-14-2)*
Isophorone (78-59-1)*	2,6-Dinitrotoluene (606-20-2)*

Federal agencies, states, municipalities, universities, private laboratories, and industry should find this evaluative study of assistance in monitoring and controlling pollution in the environment.

Robert L. Booth
Acting Director, EMSL-Cincinnati

*CAS Registry Number

ABSTRACT

An interlaboratory study in which 18 laboratories participated was conducted to provide precision and accuracy statements for the proposed EPA Method 609 for measuring concentrations of the Category 4 chemicals nitrobenzene, isophorone, 2,4-dinitrotoluene and 2,6-dinitrotoluene in municipal and industrial aqueous discharges. Method 609 involves solvent extraction of the pollutants with methylene chloride followed by Florisil cleanup and subsequent gas chromatographic analysis of the four subject compounds using flame ionization and electron capture detection techniques.

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The study was conducted at the request of the Environmental Protection Agency, Quality Assurance Branch, Environmental Monitoring and Support Laboratory, Cincinnati, Ohio under EPA Contract No. 68-03-2624. This report covers a period from September 13, 1978 to October 31, 1983, and work was completed as of December 31, 1982.

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Gratitude is also expressed to various industries for their interest in the study and willingness to provide samples of appropriate wastewater effluents without which the program's objectives could not have been realized. Lastly, we thank Mr. Edward L. Berg and Robert Graves, EPA Project Officers, whose guidance and intense interest in the study contributed to the successful completion of a difficult and sometimes frustrating task.

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SECTION 1

INTRODUCTION

EPA first promulgated guidelines (1) establishing test procedures for the analysis of pollutants in 1973, following the passage of the Federal Water Pollution Control Act in 1972 by Congress. Pursuant to the amendment and publication of these guidelines, EPA entered into a Settlement Agreement-the Consent Decree--which required the study and, if necessary, regulation of 65 "priority" pollutants and classes of pollutants of known or suspected toxicity to the biota. Subsequently, Congress passed the Clean Water Act of 1977(2), mandating the control of toxic pollutants discharges into ambient waters by industry.

In order to facilitate the implementation of the Clean Water Act, EPA selected 129 specific toxic pollutants, 113 organic and 16 inorganic, for initial study. The organic pollutants were divided into 12 categories based on their chemical structure. Analytical methods were developed by EPA for these 12 categories through in-house and contracted research. These analytical methods may eventually be required for the monitoring of the 113 toxic pollutants in industrial waste water effluents, as specified by the Clean Water Act of 1977.

This report describes the interlaboratory study of Method 609 which is proposed for the Category 4 chemicals: nitrobenzene, isophorone, 2,4-dinitrotoluene, and 2,6-dinitrotoluene. The primary objective of the study was to characterize the behavior of Method 609 in terms of 1) accuracy; 2) overall precision; 3) single-analyst precision; and 4) effect of water type of accuracy and precision. The study was conducted with the cooperation of 18 participating laboratories under auspices of the Environmental Monitoring and Support Laboratory (EMSL) - Cincinnati.

Each of the laboratories was supplied with six samples of the Category 4 chemicals as solutions in acetone packaged in flame-sealed glass ampules. One mL aliquots of the solutions were added to six types of test waters according to instructions. Water samples were then analyzed with and without the increment, and the added level of pollutant determined by difference. Concentrations were reported in µg/L with only one value reported for each sample.

The data were collected from the 18 laboratories according to Youden's(3) collaborative testing design. Formal statistical techniques compatible with the Youden design were used to identify outliers, estimate the method's accuracy and precision and test for the effect of water type. The formal statistical analyses were carried out using the Interlaboratory Method Validation Study (IMVS) computer program(4). The information obtained from the statistical analyses was summarized and reduced to a descriptive form for the purpose of interpretation and presentation.

Method 609 was developed in the Battelle-Columbus Laboratories (BCL) under a contract with the Physical and Chemical Methods Branch, Environmental Monitoring and Support Laboratory-Cincinnati. Method 609 is presented in Appendix A. Briefly, the method requires extraction of the pollutants with methylene chloride, Kuderna-Danish concentration, followed by Florisil cleanup and subsequent gas chromatographic analysis of the four subject compounds. Nitrobenzene and isophorone are measured using flame ionization detection and 2,4-dinitrotoluene and 2,6-dinitrotoluene are measured using electron capture detection.

SECTION 2

SUMMARY

The Interlaboratory Method Study of an analytical process such as Method 609 involves characterizing the accuracy and precision of the method over a wide range of working conditions. Accuracy is directly related to mean recovery and precision is related to both the overall variation and the single-analyst variation of the method.

A range of typical working conditions was introduced into the study by varying both the concentration levels of the analytes spiked into the sample test water and by changing the type of test water. For each analyte, three concentration levels (low, medium, and high) were used with each of six different test waters (distilled water, tap water, surface water, and three industrial wastewater effluents).

For purposes of summarizing the accuracy of Method 609, the following equation was determined for each effluent:

$$X = a + b \cdot C$$

where X denotes the mean recovery and C the concentration level of the analyte. The precision was summarized for each effluent by the equations

$$S = d + e \cdot X \text{ and } SR = f + g \cdot X$$

where S denotes the overall standard deviation and SR the single-analyst standard deviation.

The data reported by the 18 participating laboratories were used to estimate the coefficients a, b, d, e, f, and g for these equations for each

effluent. Generally, the intercepts (a,d,f) were judged to be negligible. Therefore, the mean recovery X is directly related to the concentration level C by $X = b \cdot C$, and the percent recovery is estimated by b x 100.

Similarly, the overall and single-analyst standard deviation are directly related to the mean recovery X by $S = e \cdot X$ and $SR = g \cdot X$ respectively. Therefore, the relative standard deviations (S/X) x 100 and (SR/X) x 100 are estimated by e x 100 and by g x 100, respectively.

These statistics were calculated for each effluent used in this study, and the results are summarized in the following tables.

TABLE 1. PERCENT RECOVERY STATISTICS* (b x 100)

Compound	Water 1	Water 2	Water 3	Water 4	Water 5	Water 6
Nitrobenzene	60	71	69	68	61	75
Isophorone	49	66	59	67	62	62
2,4-Dinitrotoluene	65	65	59	64	60	64
2,6-Dinitrotoluene	66	66	63	67	68	67

* Water Legend

1 - Distilled water
2 - Tap water
3 - Surface water (each lab supplied site specific water)
4 - Wastewater (C-44)
5 - Wastewater (C-45)
6 - Wastewater (C-46)

TABLE 2. OVERALL PERCENT RELATIVE STANDARD DEVIATION ASSOCIATED WITH S (e x 100)

Compound	Water 1	Water 2	Water 3	Water 4	Water 5	Water 6
Nitrobenzene	37	45	43	26	38	26
Isophorone	46	60	46	33	52	54
2,4-Dinitrotoluene	37	35	34	28	32	29
2,6-Dinitrotoluene	36	37	34	25	25	29

TABLE 3. SINGLE-ANALYST PERCENT RELATIVE STANDARD DEVIATION ASSOCIATED WITH SR (g x 100)

Compound	Water 1	Water 2	Water 3	Water 4	Water 5	Water 6
Nitrobenzene	25	30	37	18	20	16
Isophorone	28	45	37	27	22	26
2,4-Dinitrotoluene	20	25	27	18	16	22
2,6-Dinitrotoluene	19	23	24	15	13	20

In addition to summarizing the accuracy and precision of Method 609, the following observations were made based on the data:

- The method has a pronounced negative bias for all compounds at all concentration levels in all effluents.
- In general, there are no differences of practical importance in accuracy or precision due to water types.

SECTION 3

DESCRIPTION OF STUDY

SELECTION OF PARTICIPATING LABORATORIES

Potential participants identified from a list of 100 laboratories provided by EPA were informed of the impending study. Forty-one laboratories responded to the request for technical and cost proposals. Proposals were carefully reviewed and then ranked on the basis of technical experience and facilities. The laboratories selected for awards represented a mix of those showing average to above average analytical capabilities and are listed below:

Analytical Development Company
1875 Willow Park Way
P.O. Box 744
Monument, CO 80132

Environmental Protection Agency, EMSL
Cincinnati, OH 43268

Environmental Research Group, Inc.
117 N. First
Ann Arbor, MI 48103

Environmental Science and Engineering
P.O. Box 1354
Gainesville, FL 32604

Gulf South Research Institute
P.O. Box 26518
New Orleans, LA 70186

Mead Technology Laboratories
P.O. Box 12652
Research Triangle Park, NC 27709

Metpath
One Malcom Avenue
Teterboro, NJ 07608

Radian Corporation
8500 Shoal Creek Boulevard
P.O. Box 9948
Austin, TX 78766

Raltech Scientific Services, Inc.
P.O. Box 7545
Madison, WI 53707

Science Applications, Inc.
1200 Prospect Street
P.O. Box 2351
La Jolla, CA 92038

Southern Research Institute
2000 Ninth Avenue, S.
Birmingham, AL 35205

Southwest Research Institute
8500 Culebra Road
P.O. Drawer 25810
San Antonio, TX 78284

Syracuse Research Laboratory
Merrill Lane
Syracuse, NY 13210

Midwest Research Institute
425 Volker Boulevard
Kansas City, MO 64110

Monsanto Research Corporation
P.O. Box 8, Sta. B
Dayton, OH 45407

Systems, Science, and Software
3398 Carmel Mountain Road
San Diego, CA 92121

West Coast Technical Service
17605 Fabrica Way, Suite D
Cerritos, CA 90701

Wilson Laboratories
525 North Ninth
Salina, KS 67401

TEST DESIGN

The test design was patterned after Youden's original plan(3) for collaborative evaluation of precision and accuracy for analytical methods. According to Youden's design, samples are analyzed in pairs, with each sample of a pair having a slightly different concentration of the constituent of interest. The analyst is directed to do a single analysis and report one value for each sample, as if for a normal routine sample.

Prior to the start of the evaluation, a preliminary study was conducted to enable the participants to gain experience with the analytical and sample handling procedures. Each analyst analyzed one trial Youden pair sample and then attended a prestudy conference at EPA in Cincinnati, Ohio, to discuss the findings, the method, and the factors that could affect the quality of data. The major discussions concerned Florisil cleanup of solvent extracts and gas chromatographic conditions. A number of recommendations were offered for improving method performance. Modifications to the method approved by EPA are summarized in Appendix B.

Test samples were prepared as liquid concentrates in sealed glass ampules and presented to the analyst with complete instructions. The analyst was required to add an aliquot of each concentrate to a volume of distilled water and to a volume of each of the five water types described below. The analysis in distilled water was used to evaluate the analyst's ability to use the method on a sample free of interferences. Analyses in other water types were intended to reveal effects of various chemical matrices on the method's performance. Major elements of the test design were:

1. Three Youden pairs of samples were analyzed for each parameter and the concentrations within each pair deviated at least ± 5 percent but

no more than ±20 percent from the mean of the pair. The three Youden pairs were spread over a usable and realistic range, the lowest pair being slightly above the minimum detection limit.

2. Samples of approximately 2 mL were supplied as liquid concentrates in acetone contained in 10 mL glass ampules. One-mL aliquots of the concentrates were added to the test waters according to the instructions. Water samples including distilled water were analyzed with and without added increment and the added level determined by difference. Concentrations were reported in terms of µg/L with only one value reported for each sample.
3. Analyses were conducted in six types of water as follows:
   a Distilled water
   b A municipal drinking water
   c. A surface water vulnerable to synthetic chemical contamination as from a river
   d. Three industrial wastewaters from industries that normally would be regulated for the priority pollutants under study.
4. The participating laboratories were provided with a detailed write-up of methods of analysis, chemical standards required for calibration studies and samples of the three industrial wastewaters. Each participating laboratory was responsible for securing samples of the other three test waters.

SECTION 4

EXPERIMENTAL PROCEDURES

PREPARATION OF YOUDEN PAIR CONCENTRATES

Stock solutions of the Category 4 compounds (nitrobenzene, isophorone, 2,4-dinitrotoluene and 2,6-dinitrotoluene) were prepared by dissolving accurately weighed amounts of the chemicals in acetone. The sample concentrates were then prepared by diluting measured amounts of the stock solutions to larger volumes. As noted, the concentration of a given compound in each Youden pair was adjusted so that it differed by at least $\pm$ 5 percent, but was no greater than $\pm$ 20 percent from the mean of the pair.

The concentrations of the diluted solutions were confirmed by gas chromatography using direct sample injection. Chromatographic conditions were similar to those described in Method 609. Sample concentrates of approximately 2 mL of the diluted solutions were then prepared in 10 mL glass ampules and flame-sealed.

When diluted with test water according to instructions, the calculated concentrations of the Category 4 compounds in the diluted sample expressed as µg/L are given in Table 4.

TABLE 4. TRUE VALUES[a] OF CATEGORY 4 COMPOUNDS IN TEST WATERS

Component	Ampul Number					
	1	2	3	4	5	6
Nitrobenzene	210.0	425.0	35.0	515.0	25.0	175.0
Isophorone	150.0	475.0	25.0	400.0	35.0	200.0
2,4-Dinitrotoluene	10.0	55.0	1.4	45.0	1.0	12.0
2,6-Dinitrotoluene	10.0	60.0	1.4	50.0	1.0	12.0

(a) In µg/L.

STABILITY OF YOUDEN PAIR CONCENTRATES

The stability of the Youden pairs of Category 4 compounds was studied over a 90-day period. Triplicate samples of each Youden pair concentrate were selected at random and analyzed at 0, 45, and 90 days. The stability of the samples was considered satisfactory. At the end of the 90-day period, overall deviation of the analyzed values from the true values did not exceed $\pm$ 5 percent at each concentration level.

COLLECTION OF INDUSTRIAL WASTEWATER EFFLUENTS

Chemical industries producing Category 4 compounds or utilizing them in chemical processes were identified from Synthetic Organic Chemicals - U.S. Production and Sales 1974-77, U.S. International Trade Commission, and the 1979 Directory of Chemical Producers in the United States.

Since Method 609 may eventually be used by industries seeking permits issued by the National Pollutant Discharge Elimination System under the Clean Water Act, plants using best available technology in their wastewater treatment facilities were selected for sampling. Attempts were made to obtain wastewater samples from both users and producers of the various category compounds. The appropriateness of a particular company's wastewater was first assessed by discussions with technical personnel of that company. If on the basis of these discussions, it appeared that the plant's effluent might be suitable for the program, a 1-gallon sample of the effluent was sent to BCL for a preliminary analysis. The effluent was judged to be suitable for the method study if the analysis showed no major interferences or high background of the chemical parameters of interest that might nullify analytical data obtained for the lowest Youden pair concentrates. Approximately 55 gallons of acceptable wastewater effluents were collected in stainless steel drums at the plant sites by plant or BCL personnel and delivered to BCL by truck. Samples of wastewater were analyzed at BCL before and after spiking with the various Category 4 compounds. If the results of these analyses were satisfactory, 1-quart samples of the effluent were prepared for shipment to the participating laboratories. The contents of the drums were stirred vigorously during the bottling operation to ensure sample homogeneity. The 1-quart samples were identified by coded labels as

C-44, C-45, or C-46. A brief description of plant source and methods of wastewater treatment are given below. The results of BCL's analysis of the wastewater samples are given in Table 5.

Wastewater C-44 (SIC Code #2869*)--Effluent from a plant producing nitroaromatics and aromatic amines. Wastewater treatment includes biological treatment in an activated sludge plant followed by tertiary carbon treatment and then discharge into a river.

Wastewater C-45 (SIC Code #2865*)--Effluent from plant producing a variety of nitroaromatic and aromatic amines including nitrobenzene, 2,4-dinitrotoluene and 2,6-dinitrotoluene. Wastewater stream is first neutralized with lime, filtered, and then treated in an activated secondary sludge plant. Following clarification and chlorination the treated wastestream is discharged into a creek tributary to a river.

Wastewater C-46 (SIC Code #2869*)--Wastewater stream is from a plant producing various organic chemicals including isophorone. Process water is discharged into API separators. Any oil fraction is recovered and reused. The water fraction passes through an activated sludge plant and a secondary clarifier and then discharged into a creek tributary to a river.

---

* Standard Industrial Classification Code Number

TABLE 5. BACKGROUND ANALYSES OF WASTEWATER SAMPLES FOR CATEGORY 4 COMPOUNDS, µg/L

Compound	Sample C-44	Sample C-45	Sample C-46
Nitrobenzene	<5	<5	<5
Isophorone	<5	<5	<5(a)
2,4-Dinitrotoluene	<1	<1	<1
2,6-Dinitrotoluene	<1	<1	<1

(a) Sample contains possible interference which elutes slightly before isophorone peak.

DISTRIBUTION OF SAMPLES

Each laboratory was provided with the following materials:

(1) Six Youden pair samples of each of three concentration levels, a total of 36 ampule samples

(2) Seven, 1-quart samples of three types of industrial wastewater effluents yielding a total of 21 samples

(3) One-gram standards of nitrobenzene, isophorone, 2,4-dinitrotoluene and 2,6-dinitrotoluene

(4) A copy of Method 609

(5) A form for reporting data

(6) A questionnaire requesting description of difficulties encountered with the analytical method and suggestions for improvement of the method.

The laboratories were instructed to add the sample concentrates to the test waters by the following procedure:

Place a magnetic stirbar in the sample bottle, add 1 mL of the sample concentrate, then cap and stir 15 minutes using a magnetic stirrer. Transfer the contents of the bottle to a 2-liter separatory funnel and proceed with the analysis as described in Method 609, Nitroaromatics and Isophorone. In calculating results, assume the volume of the sample to be one liter.

TREATMENT OF DATA

The study's objective was met through the use of statistical analysis techniques designed to extract and summarize the relevant information about accuracy and precision from the data reported by the participating laboratories. The statistical techniques employed in the data reduction process are similar to ASTM techniques.

The algorithms required to perform the statistical analyses have been integrated into a system of computer programs referred to as IMVS. The analyses performed by IMVS include several tests for the rejection of outliers (laboratories and individual data points), summary statistics by concentration level for mean recovery (accuracy), overall and single-analyst standard deviation (precision), determination of the linear relationship between mean recovery and concentration level, determination of the linear relationship between the precision statistics and mean recovery, and a test for the effect of water type on accuracy and precision.

A detailed description of each of the statistical analysis procedures is presented below.

REJECTION OF OUTLIERS

Since the objective of the statistical analyses is to summarize the general behavior of the method in terms of accuracy and precision, it is important to identify data points which are inconsistent with the majority of the data. These data points should be deleted from the analysis because they can lead to values of summary statistics which are not representative of the general behavior of the method. However, some erratic behavior in the data may be directly related to some facet of the method under the study. Therefore, inconsistent data points should not be removed indiscriminately, and any points that are removed should be clearly identified, since further investigation of the analytical conditions related to the outliers might be of value. In some cases the data points which are deleted may actually be closer to the true value than the retained data. This is not inconsistent since outliers are judged relative to the average value of the data and not with respect to the true value. Data rejected as outliers for this study as

a result of any of the following tests for outliers have been identified by the symbol "*" in the raw data tables.

Youden's Laboratory Ranking Procedure

In some cases, the analytical values reported by a specific laboratory are so consistently high or low that a large systematic error may be attributed to that laboratory. These data are not representative of the method and should be rejected. Youden's(3) ranking test for outlying laboratories was applied separately to data from each of the waters used in this study. Since six water types were used in this study, the laboratory ranking procedure was applied to these six different subsets of the data. Each laboratory ranking test was performed at the 5 percent level of significance.

The Youden laboratory ranking procedure requires a complete set of data from every laboratory within a given water type. Missing data from laboratory i for water type j were replaced by the following procedure. Letting X_{ijk} denote the reported measurement from laboratory i for water type j and concentration level C_k, it is assumed that

$$X_{ijk} = \beta_j \cdot C_k^{\gamma_j} \cdot L_i \cdot \varepsilon_{ijk}$$

where β_j and γ_j are fixed parameters which determine the effect of water type j, L_i is the systematic error due to laboratory i and ε_{ijk} is the random within laboratory error. Taking natural logarithms, it follows that

$$\ell n\, X_{ijk} = \ell n\, \beta_j + \gamma_j\, \ell n\, C_k + \ell n\, L_i + \ell n\, \varepsilon_{ijk}$$

which is a linear regression model with dependent variable $\ell n\, X_{ijk}$ and independent variable $\ell n\, C_k$. Details and justification for this model are discussed in the section "Comparison of Accuracy and Precision Across Water Types".

The natural logarithms of the individual laboratory's data were regressed against the natural logarithms of the true concentration levels for the six ampules in each water type. The predicted values $\ell n\, \hat{X}_{ijk}$ were obtained from the regression equation, and the missing values for X_{ijk} were estimated by $\hat{X}_{ijk} = \exp(\ell n\, \hat{X}_{ijk})$, where exp(x) denotes the constant e raised to the power X.

If the ranking test rejected a laboratory for a specific water type, then all the laboratory's data for that water type were rejected as outliers. The rejected values were excluded from all the remaining analyses. In addition, after completion of the laboratory ranking procedure, the predicted values created to fill in for the missing data were rejected and excluded from further analyses for all laboratories.

Individual Outliers

The data remaining after the laboratory ranking procedure were grouped by water type. For each water type, the data were broken down into six subsets defined by the six concentration levels (ampules) used in the study. For each subset of the data, all missing zero, "less than," and "nondetect" data were rejected. Next, the test for individual outliers constructed by Thompson(5), and suggested in the ASTM Standard Practice D2777-77, was applied to the data using a 5 percent significance level. If an individual data point was rejected based on this test, it was removed from the subset, and the test was repeated using the remaining data in the subset. This process was continued until no additional data could be rejected.

STATISTICAL SUMMARIES DATA

Several summary statistics were calculated using the data remaining for each concentration level after the outlier rejection tests were performed. These summary statistics include: the number of retained data points, the mean recovery, accuracy as a percent relative error, the absolute overall standard deviation, the percent relative overall standard deviation, the absolute single-analyst standard deviation, and the percent relative single-analyst standard deviation. The basic formulas used to calculate these statistics are presented below (X_1, X_2,..., X_n denote the values of the n retained data points for a specific concentration level):

Mean Recovery (X):

$$X = \frac{1}{n} \sum_{i=1}^{n} X_i$$

The usual concentration notation for mean recovery is $\bar{X}$. However, the symbol X is used in this report to be consistent with the IMVS output.

Accuracy as a Percent Relative Error:

$$\text{Percent RE} = \frac{X - \text{True Value}}{\text{True Value}} \times 100$$

Overall Standard Deviation:

and

$$S = \sqrt{\frac{1}{n-1} \sum_{i=1}^{n} (X_i - X)^2}$$

Percent Relative Overall Standard Deviation:

$$\text{Percent RSD} = \frac{S}{X} \times 100$$

The overall standard deviation S indicates the precision associated with measurements generated by a group of laboratories. This represents the broad variation in the data collected in an interlaboratory study. However, a measure of how well an individual analyst can expect to perform in his own laboratory is another important measure of precision. This single-analyst precision, denoted by SR, was estimated for each Youden pair by

$$SR = \sqrt{\frac{1}{2(m-1)} \sum_{i=1}^{m} (D_i - \bar{D})^2}$$

where

m = the number of complete sets of Youden pair observations remaining after outliers have been removed,

D_i = the difference between the observations in the ith Youden pair

and

$\bar{D}$ = average of the D_i values.

The percent relative single-analyst standard deviation was calculated by

$$\text{Percent RSD-SR} = \frac{SR}{X^*} \times 100$$

where X* is the average of the two mean recovery statistics corresponding to the two concentration levels defining the particular Youden pair.

These summary statistics provide detailed information on the accuracy and precision of the data obtained for each concentration level. One objective of the statistical analysis of the data is to summarize the information about accuracy and precision which is contained in the statistics.

A systematic relationship often exists between the mean recovery (X) and the true concentration level (C) of the analyte in the sample. In addition there are often systematic relationships between the precision statistics (S and SR) and the mean recovery (X). Usually these systematic relationships can be adequately approximated by a linear relationship (i.e. by a straight line). Once these straight lines are established, they can be used to conveniently summarize the behavior of the method within a water type, and they can aid in comparing the behavior of the method across water types. In addition they can be used to obtain estimates of the accuracy and precision at any concentration level within the applicable range studied. They can also be used to predict the behavior of the method when used under similar conditions. These important relationships are discussed below.

STATEMENT OF METHOD ACCURACY

The accuracy of the method is characterized by the relationship of the mean recovery (X) to the true concentration (C) of the analyte in the water sample. In order to obtain a mathematical expression for this relationship, a regression line of the form

$$X = a + b \cdot C \qquad (1)$$

was fitted to the data by regression techniques.

The true concentration values often vary over a wide range. In such cases, the mean recovery statistics associated with the larger

concentration values tend to dominate the fitted regression line producing relatively larger errors in the estimates of mean recovery at the lower concentration values. In order to eliminate this problem, a weighted least squares technique was used to fit the mean recovery data to the true concentration values. The weighted least squares technique was performed by dividing both sides of Equation (1) by C resulting in Equation (2)

$$\frac{X}{C} = a \cdot \frac{1}{C} + b \qquad (2)$$

The (X/C) values were regressed against the (1/C) values using ordinary least squares to obtain estimates for the values of a and b. (This is equivalent to performing a weighted least squares with weights $w = 1/C^2$; see Reference (6), page 108 for details.) Equation (2) can easily be converted to the desired relationship given by Equation (1). The intercept (b) from Equation (2) becomes the slope (b) for Equation (1) and slope (a) from Equation (2) becomes the intercept (a) for Equation (1). Equation (1) can be used to calculate the percent recovery over the applicable range of concentrations used in the study.

The percent recovery is given by

$$\text{Percent Recovery} = \left[\frac{a + b \cdot C}{C}\right] \times 100 = \left[\frac{a}{C} + b\right] \times 100 \qquad (3)$$

If the absolute value of the ratio (a/C) is small relative to the slope (b) for the low concentration levels used in the study, then the percent recovery can be approximated by b x 100. For example, suppose the true concentration values range from 25 µg/L to 515 µg/L, and the fitted line is given by $X = 0.20 + 0.85 \cdot C$. The percent recovery would be approximated by 0.85 x 100 = 85 percent over the specified range of 25 µg/L to 515 µg/L.

If the ratio (a/C) is not small relative to the slope (b), then the percent recovery depends upon the true concentration (C), and it must be evaluated at each concentration value within the specified range.

STATEMENT OF METHOD PRECISION

The precision of the method is characterized by the relationships between precision statistics (S and SR) and mean recovery (X). In order to obtain a mathematical expression for these relationships, regression lines of the form

$$S = d + e \cdot X \tag{4}$$

and

$$SR = f + g \cdot X^* \tag{5}$$

were fitted to the data by regression techniques.

As discussed previously with respect to accuracy, the values of X and X* often vary over a wide range. In such cases, the standard deviation statistics associated with the larger mean recovery values will dominate the regression lines. This will produce relatively larger errors in the estimates of S and SR at the lower mean recovery values. Therefore, a weighted least squares technique was also used to establish the values of the parameters d, e, f, and g in Equations (4) and (5). The weighted least squares technique was performed by dividing both sides of Equation (4) by X resulting in Equation (6)

$$\frac{S}{X} = d \cdot \frac{1}{X} + e \quad , \tag{6}$$

and by dividing both sides of Equation (5) by X* resulting in Equation (7)

$$\frac{SR}{X^*} = f \cdot \frac{1}{X^*} + g \quad . \tag{7}$$

The (S/X) values were regressed against the (1/X) values and the (SR/X*) values were regressed against the (1/X*) values using ordinary least squares to obtain estimates for the parameters d, e, f, and g.

Equations (4) and (5) were obtained from Equations (6) and (7) in a manner similar to that discussed for mean recovery. The slope (d) for Equation (6) is the intercept (d) for Equation (4), and the intercept (e) for Equation (6) is the slope (e) for Equation (4). Similarly, the slope (f) for

Equation (7) is the intercept (f) for Equation (5), and the intercept (g) for Equation (7) is the slope (g) for Equation (5).

Given Equations (4) and (5), the percent relative overall standard deviation and the percent relative single-analyst standard deviation are

$$\text{Percent RSD} = \left[\frac{d}{X} + e\right] \times 100 \qquad (8)$$

and

$$\text{Percent RSD-SA} = \left[\frac{f}{X^*} + g\right] \times 100 \qquad (9)$$

respectively. If the absolute value of the ratio (d/X) is small relative to the slope (e) then the percent relative overall standard deviation can be approximated by (e x 100) over the applicable range of mean recovery values. Similarly if the ratio (f/X*) is small relative to the slope (g), then the percent relative single-analyst standard deviation can be approximated by (g x 100) over the applicable range of mean recovery values. If the ratios (d/X) and (f/X*) are not small relative to the slopes (e) and (f), then the percent relative standard deviations depend upon the values of the mean recovery statistics X and X*, and they should be evaluated separately for each value of X and X*.

COMPARISON OF ACCURACY AND PRECISION ACROSS WATER TYPES

It is possible that the accuracy and precision of Method 609 depend upon the type of water being analyzed. The summary statistics X, S, and SR are calculated separately for each concentration level within each water type. They can be compared across water types in order to obtain information about the effects of water type on accuracy and precision. However, the use of these summary statistics in this manner has several disadvantages. First, it is cumbersome since there are 36 mean recovery statistics (X) (6 concentrations x 6 waters), 36 precision statistics (S), and 18 precision statistics (SR) calculated for each compound. Comparison of these statistics across concentration levels and across water types becomes unwieldy. Second, the statistical properties of this type of comparison procedure are difficult to determine. Finally, due to variation associated with X, S, and SR,

comparisons based on these statistics can lead to inconsistent conclusions about the effect of water type. For example, distilled water may produce a significantly lower value than surface water for the precision statistic S at a high concentration, but a significantly higher value for S at a low concentration.

An alternative approach, described in detail(7) has been developed to test for the effects of water type. This alternative approach is based on the concept of summarizing the average effect of water type across concentration levels rather than studying the local effects at each concentration level. If significant differences are established by this alternative technique, then the summary statistics can be used for further local analysis.

The test for the effect of water type is based on the following statistical model. If X_{ijk} denotes the measurement reported by laboratory i, for water type j, and ampule k, then

$$X_{ijk} = \beta_j \cdot C_k^{\gamma_j} \cdot L_i \cdot \varepsilon_{ijk} \quad \begin{matrix} i = 1,2,\ldots, n \\ j = 1,2,\ldots, 6 \\ k = 1,2,\ldots, 6 \end{matrix} \quad . \qquad (10)$$

The model components β_j and γ_j are fixed parameters which determine the effect of water type j on the behavior of the observed measurements (X_{ijk}). The parameter C_k is the true concentration level associated with ampule k. The model component L_i is a random factor which accounts for the systematic error associated with laboratory i. The model component ε_{ijk} is the random factor which accounts for the within-laboratory error.

The model is designed to approximate the global behavior of the data. The multiplicative structure was chosen because of two important properties. First, it allows for a possible curvilinear relationship between the data (X_{ijk}) and the true concentration level C_k through the use of the exponent γ_j on C_k. This makes the model more flexible in comparison to straight line models. Second, as will be seen below, there is an inherent increasing relationship between the variability in the data and the concentration level C_k in this model. This property is important because it is typical of interlaboratory data collected under conditions where the true concentration levels vary widely.

Accuracy is related directly to the mean recovery or expected value of the measurements (X_{ijk}). The expected value for the data modeled by Equation (10) is

$$E(X_{ijk}) = \beta_j \cdot C_k^{\gamma_j} \cdot E(L_i \cdot \varepsilon_{ijk}) \qquad (11)$$

Precision is related to the variability in the measurements (X_{ijk}). The variance of the data modeled by Equation (10) is

$$Var(X_{ijk}) = \left[\beta_j C_k^{\gamma_j} \right]^2 Var(L_i \cdot \varepsilon_{ijk}) \qquad (12)$$

which is an increasing function of C_k.

The effect of water type on the accuracy and precision of Method 609 is determined by the values of the parameters (β_j) and (γ_j) in Equations (11) and (12). If the (β_j) and (γ_j) vary with j (i.e. vary across water type), then the accuracy and precision of the method also vary across water type.

In order to determine if these parameters do vary across water type and to compare their values, they must be estimated from the laboratory data using regression techniques. Equation (10) represents the basic model. However, taking natural logarithms of both sides of Equation (10), the following straight line regression model is obtained

$$\ln X_{ijk} = \ln \beta_j + \gamma_j \ln C_k + \ln L_i + \ln \varepsilon_{ijk} \qquad (13)$$

which can be analyzed using standard linear model analysis techniques. The parameter $\ln \beta_j$ is the intercept and γ_j the slope of the regression line associated with water type j. It is assumed that $\ln L_i$ is normally distributed with mean 0 and variance σ_L^2, and that $\ln \varepsilon_{ijk}$ is normally distributed with mean 0 and variance σ_ε^2, and that the ($\ln L_i$) and ($\ln \varepsilon_{ijk}$) terms are independent.

Based on Equation (13), the comparison of water types reduces to the comparison of straight lines. Distilled water is viewed as a control, and each of the remaining lines is compared directly to the line for distilled water.

Using the data on the log-log scale and regression techniques, the parameters $\ln \beta_j$ (and hence β_j) and γ_j can be estimated. The estimates are then used to test the null hypothesis that there is no effect due to water type. The formal null and alternative statistical hypotheses H_0 and H_A are given by

$$H_0: \ \ln \beta_j - \ln \beta_1 = 0 \text{ and } \gamma_j - \gamma_1 = 0 \text{ for } j = 2,3,4,5,6$$

versus

$$H_A: \ \ln \beta_j - \ln \beta_1 \neq 0 \text{ and/or } \gamma_j - \gamma_1 \neq 0 \text{ for some } j = 2,3,4,5,6 \ .$$

The test of null hypothesis H_0 against the alternative hypothesis H_A is based on an F-statistic derived from standard linear model theory. The probability of obtaining a value of an F-statistic as large as the value which was actually observed (F OBS), denoted by P(F > F OBS), is calculated under the assumption that H_0 is true. The null hypothesis H_0 is rejected in favor of H_A if P(F> F OBS) is less than 0.05.

If H_0 is rejected, then some linear combination of the differences $\ln \beta_j - \ln \beta_1$ and $\gamma_j - \gamma_1$ is statistically different from zero. However, this does not guarantee there will be a statistically significant direct effect attributable to any specific water type since the overall F test can be overly sensitive to a minor systematic effect common to several water types. The effect due to a specific water type is judged to be statistically significant only if one of the differences $\ln \beta_j - \ln \beta_1$ and/or $\gamma_j - \gamma_1$ is statistically different from zero. This is determined by checking the simultaneous 95 percent confidence intervals which are constructed for each of these differences. Each true difference can be stated to lie within its respective confidence interval with 95 percent confidence. If zero is contained within the confidence interval, then there is no evidence that the corresponding difference is significantly different from zero.

If at least one of the confidence intervals for the differences $\ln \beta_j - \ln \beta_1$ or $\gamma_j - \gamma_1$ fails to include zero, then the statistical significance of the effect due to water type has been established. However, establishment of a statistically significant effect due to water type does not necessarily mean that the effect is of practical importance. Practical importance is related to the size and interpretation of the difference.

The interpretation of the differences involves comparing the mean recovery and standard deviation of the (X_{ijk}) data for each water type to the mean

recovery and standard deviation obtained for distilled water. These comparisons are made on a relative basis. The mean recovery for water type j is given by Equation (11). The mean recovery for water type j is compared to that for distilled water (j=1) on a relative basis by the ratio

$$\frac{E(X_{ijk})}{E(X_{i1k})} = \frac{\beta_j C_k^{\gamma_j} E(L_i \cdot \varepsilon_{ijk})}{\beta_1 C_k^{\gamma_1} E(L_i \cdot \varepsilon_{i1k})} = \frac{\beta_j}{\beta_1} C_k^{\gamma_j - \gamma_1} \quad . \tag{14}$$

(The ratio of the standard deviations would be equivalent to Equation (14) and therefore the interpretation of the effect on precision is the same as that for the effect on mean recovery.)

The ratio in Equation (4) is a measure of the relative difference in mean recovery between water type j and distilled water. It is composed of two parts (a) β_j/β_1, which is independent of the true concentration level (i.e. the constant bias), and (b) $C_k^{\gamma_j - \gamma_1}$ which depends upon the true concentration level (i.e. the concentration dependent bias). If $\gamma_j - \gamma_1$ is zero, then the relative difference in mean recovery is just β_j/β_1, which is independent of concentration level C_k. It can then be stated that the mean recovery of water type j is (β_j/β_1) x 100 percent of the mean recovery for distilled water. If $\gamma_j - \gamma_1$ is not zero, then the mean recovery of water type j is $((\beta_j/\beta_1).C_k^{\gamma_j - \gamma_1})$ x 100 percent of that for distilled water, and therefore depends upon the true concentration level C_k.

In order to illustrate these points, consider the following example. Suppose that a significant F-value has been obtained, and the confidence intervals for all the differences contain zero except for water type 5. For water type 5, the point estimate for $\ln \beta_5 - \ln \beta_1$ is -0.38 and the confidence interval for $\ln \beta_5 - \ln \beta_1$ is (-0.69, -0.07). The point estimate for $\gamma_5 - \gamma_1$ is 0.07, and the confidence interval for $\gamma_5 - \gamma_1$ is (-0.04, 0.18). In this case, a statistically significant effect due to water type has been established which involves only water type 5. The practical significance of this effect is judged by considering Equation (14). The ratio of mean recoveries for water type 5 and distilled water is given by

$$\frac{E(X_{i5k})}{E(X_{i1k})} = \frac{\beta_5}{\beta_1} C_k^{\gamma_5 - \gamma_1} \tag{15}$$

and the ratio of the standard deviations is given by

$$\sqrt{\frac{\mathrm{Var}(X_{ijk})}{\mathrm{Var}(X_{ilk})}} = \frac{\beta_5}{\beta_1} C_k^{\gamma_5 - \gamma_1} \tag{16}$$

Since the confidence interval for $\gamma_5 - \gamma_1$ contains zero, this difference is assumed to be insignificant and is set to zero. Therefore, Equations (15) and (16) reduce to β_5/β_1. the point estimate for $\ln \beta_5 - \ln \beta_1$ was -0.38. Therefore, the point estimate for β_5/β_1 is 0.68, and the mean recovery for water type 5 is estimated to be 68 percent of the mean recovery for distilled water. Similarly, the standard deviation for the data for water type 5 is estimated to be 68 percent of the standard deviation for distilled water. Since the 95 percent confidence interval for $\ln \beta_5 - \ln \beta_1$ was (-0.69, -0.07), any value in the interval (0.50, 0.93) is a reasonable estimate for β_5/β_1, and the mean recovery (standard deviation) for water type 5 can be claimed to be from 50 percent to 93 percent of the mean recovery (standard deviation) for distilled water. The practical significance of the effect due to water type 5 would depend upon the importance of a mean recovery (standard deviation) which is between 50 percent and 93 percent of the mean recovery (standard deviation) observed for distilled water.

SECTION 5

RESULTS AND DISCUSSION

The statistical analysis procedures described in Section 4 have been applied to the raw data shown in Appendix C for the 18 laboratories participating in this interlaboratory study. The results of those analyses with respect to the performance of Method 609 are discussed in this section.

STATISTICAL SUMMARIES

The basic summary statistics discussed in Section 4 were calculated for each of the compounds nitrobenzene, isophorone, 2,4-dinitrotoluene and 2,6-dinitrotoluene and are summarized in Tables 6, 7, 8, and 9. The number of outliers for each data set as determined by the ranking and individual outlier test ranged from one to seven, and averaged about three outliers per data set. For all data for the four compounds, 19 percent of the data was rejected.

REGRESSION EQUATIONS

Using the values contained in the summary statistics for the true concentrations, mean recoveries(X and X*), overall standard deviations (S), and single-analyst standard deviations (SR), the regression lines given by Equations 1, 4, and 5 were obtained for each compound and water type. These regression lines are summarized in Table 10.

EFFECTS OF WATER TYPE

The multiplicative model (Equation 10) was fitted separately to the data for each compound in order to test for the effects due to water type. These

TABLE 6. STATISTICAL SUMMARY FOR NITROBENZENE ANALYSES BY WATER TYPE

	WATER 1		WATER 2		WATER 3		WATER 4		WATER 5		WATER 6	
LOW YOUDEN PAIR	3	5	3	5	3	5	3	5	3	5	3	5
NUMBER OF DATA POINTS	14	14	17	15	14	14	15	14	15	15	13	14
TRUE VALUE UG/L	35.00	25.00	35.00	25.00	35.00	25.00	35.00	25.00	35.00	25.00	35.00	25.00
MEAN RECOVERY	20.56	17.90	26.15	16.74	24.33	15.62	24.07	16.49	23.07	17.37	26.46	16.89
ACCURACY AS % REL ERROR	-41.26	-28.41	-25.30	-33.05	-30.49	-37.51	-31.23	-34.03	-34.07	-30.51	-24.40	-32.43
OVERALL STD DEV (S)	9.84	4.00	10.96	6.08	8.10	3.65	6.15	5.22	8.06	6.38	9.32	6.11
OVERALL REL STD DEV, %	47.86	22.33	41.92	36.35	33.30	23.37	25.54	31.64	34.93	36.72	35.22	36.16
SINGLE STD DEV, (SR)	7.29		8.30		5.01		5.69		7.23		5.87	
ANALYST REL DEV, %	37.88		38.71		25.07		28.08		35.76		27.07	
MEDIUM YOUDEN PAIR	1	6	1	6	1	6	1	6	1	6	1	6
NUMBER OF DATA POINTS	15	14	16	16	15	15	13	12	13	15	13	13
TRUE VALUE UG/L	210.00	175.00	210.00	175.00	210.00	175.00	210.00	175.00	210.00	175.00	210.00	175.00
MEAN RECOVERY	134.75	109.91	137.65	128.25	148.15	125.08	131.58	122.45	145.33	126.37	157.50	129.16
ACCURACY AS % REL ERROR	-35.83	-37.20	-34.45	-26.71	-29.45	-28.53	-37.34	-30.03	-30.79	-27.79	-25.00	-26.19
OVERALL STD DEV (S)	48.11	20.60	66.28	43.94	82.92	44.33	32.09	21.67	43.45	37.55	34.19	44.12
OVERALL REL STD DEV, %	35.70	18.75	48.15	34.26	55.97	35.44	24.39	17.69	29.89	29.71	21.71	34.16
SINGLE STD DEV, (SR)	38.89		26.65		65.50		23.35		23.30		24.49	
ANALYST REL DEV, %	31.79		20.04		47.95		18.38		17.15		17.08	
HIGH YOUDEN PAIR	2	4	2	4	2	4	2	4	2	4	2	4
NUMBER OF DATA POINTS	15	15	17	15	15	14	14	15	13	14	14	13
TRUE VALUE UG/L	425.00	515.00	425.00	515.00	425.00	515.00	425.00	515.00	425.00	515.00	425.00	515.00
MEAN RECOVERY	254.52	291.65	297.19	381.89	295.55	323.98	314.35	337.97	235.24	269.06	336.86	354.93
ACCURACY AS % REL ERROR	-40.11	-43.37	-30.07	-25.85	-30.46	-37.09	-26.04	-34.37	-44.65	-47.75	-20.74	-31.08
OVERALL STD DEV (S)	119.96	121.11	128.68	186.17	75.52	160.51	114.60	87.39	95.11	137.25	103.40	78.43
OVERALL REL STD DEV, %	47.13	41.53	43.30	48.75	25.55	49.54	36.45	25.86	40.43	51.01	30.70	22.10
SINGLE STD DEV, (SR)	59.92		137.16		77.93		62.34		65.78		57.38	
ANALYST REL DEV, %	21.94		40.39		25.16		19.11		26.09		16.59	

WATER LEGEND

1 - DISTILLED WATER
2 - TAP WATER
3 - SURFACE WATER
4 - WASTEWATER (C-44)
5 - WASTEWATER (C-45)
6 - WASTEWATER (C-46)

TABLE 7. STATISTICAL SUMMARY FOR ISOPHORONE ANALYSES BY WATER TYPE

	WATER 1		WATER 2		WATER 3		WATER 4		WATER 5		WATER 6	
LOW YOUDEN PAIR	3	5	3	5	3	5	3	5	3	5	3	5
NUMBER OF DATA POINTS	14	13	16	16	13	13	12	13	15	16	14	13
TRUE VALUE UG/L	25.00	35.00	25.00	35.00	25.00	35.00	25.00	35.00	25.00	35.00	25.00	35.00
MEAN RECOVERY	13.66	23.57	18.82	24.16	[illegible]0	21.06	15.65	22.92	15.75	27.30	33.88	23.48
ACCURACY AS % REL ERROR	-45.36	-32.65	-24.74	-30.98	[illegible].0	-39.84	-37.42	-34.52	-36.98	-21.99	35.50	-32.90
OVERALL STD DEV (S)	8.72	4.58	7.27	12.35	7.19	8.20	9.01	11.28	7.15	13.87	28.78	10.43
OVERALL REL STD DEV, %	63.83	19.44	38.62	51.13	48.91	38.93	57.62	49.22	45.36	50.81	84.94	44.41
SINGLE STD DEV, (SR)	7.81		6.80		8.04		6.84		12.04		14.19	
ANALYST REL DEV, %	41.94		31.63		44.97		35.46		55.94		49.48	

	WATER 1		WATER 2		WATER 3		WATER 4		WATER 5		WATER 6	
MEDIUM YOUDEN PAIR	1	6	1	6	1	6	1	6	1	6	1	6
NUMBER OF DATA POINTS	14	13	16	17	12	13	13	12	14	16	17	16
TRUE VALUE UG/L	150.00	200.00	150.00	200.00	150.00	200.00	150.00	200.00	150.00	200.00	150.00	200.00
MEAN RECOVERY	72.71	103.05	72.21	148.31	60.04	132.55	73.45	129.09	78.19	136.83	86.38	154.03
ACCURACY AS % REL ERROR	-51.52	-48.47	-51.86	-25.84	-59.97	-33.72	-51.03	-35.45	-47.87	-31.58	-42.42	-22.99
OVERALL STD DEV (S)	39.95	38.65	42.27	78.24	30.34	59.25	24.57	49.83	34.82	56.08	50.94	75.01
OVERALL REL STD DEV, %	54.94	37.51	58.54	52.76	50.54	44.70	33.44	38.60	44.53	40.98	58.98	48.70
SINGLE STD DEV, (SR)	31.27		38.02		43.55		41.82		24.74		42.31	
ANALYST REL DEV, %	35.58		34.49		45.22		41.30		23.01		35.20	

	WATER 1		WATER 2		WATER 3		WATER 4		WATER 5		WATER 6	
HIGH YOUDEN PAIR	2	4	2	4	2	4	2	4	2	4	2	4
NUMBER OF DATA POINTS	13	13	18	16	13	12	13	13	16	15	17	17
TRUE VALUE UG/L	475.00	400.00	475.00	400.00	475.00	400.00	475.00	400.00	475.00	400.00	475.00	400.00
MEAN RECOVERY	241.08	192.52	331.34	287.38	296.72	252.81	374.39	281.08	322.44	234.04	348.14	281.35
ACCURACY AS % REL ERROR	-49.25	-51.87	-30.24	-28.16	-37.53	-36.80	-21.18	-29.73	-32.12	-41.49	-26.71	-29.66
OVERALL STD DEV (S)	140.65	93.74	181.02	184.78	125.51	122.30	127.01	100.32	204.31	128.42	194.46	140.22
OVERALL REL STD DEV, %	58.34	48.69	54.63	64.30	42.30	48.38	33.93	35.69	63.37	54.87	55.86	49.84
SINGLE STD DEV, (SR)	53.94		156.28		85.35		53.16		81.84		80.03	
ANALYST REL DEV, %	24.88		50.52		31.06		16.22		29.41		25.43	

WATER LEGEND

1 - DISTILLED WATER
2 - TAP WATER
3 - SURFACE WATER
4 - WASTEWATER (C-44)
5 - WASTEWATER (C-45)
6 - WASTEWATER (C-46)

TABLE 8. STATISTICAL SUMMARY FOR 2,4-DINITROTOLUENE ANALYSES BY WATER TYPE

	WATER 1		WATER 2		WATER 3		WATER 4		WATER 5		WATER 6	
LOW YOUDEN PAIR	3	5	3	5	3	5	3	5	3	5	3	5
NUMBER OF DATA POINTS	12	12	15	13	16	16	16	16	14	13	14	15
TRUE VALUE UG/L	1.40	1.00	1.40	1.00	1.40	1.00	1.40	1.00	1.40	1.00	1.40	1.00
MEAN RECOVERY	1.20	.83	1.34	.68	1.17	.79	1.15	.83	.97	.55	1.18	.73
ACCURACY AS % REL ERROR	-14.11	-16.81	-4.39	-31.60	-16.56	-20.64	-18.17	-17.06	-31.07	-44.91	-16.05	-26.96
OVERALL STD DEV (S)	.46	.20	.39	.19	.56	.51	.37	.26	.39	.27	.30	.27
OVERALL REL STD DEV, %	38.52	23.50	28.86	27.84	48.00	64.45	32.01	31.11	40.60	49.12	25.56	36.36
SINGLE STD DEV, (SR)	.28		.29		.36		.27		.22		.16	
ANALYST REL DEV, %	27.62		28.20		36.30		27.77		28.75		16.89	
MEDIUM YOUDEN PAIR	1	6	1	6	1	6	1	6	1	6	1	6
NUMBER OF DATA POINTS	14	14	14	14	15	15	16	15	14	14	15	13
TRUE VALUE UG/L	10.00	12.00	10.00	12.00	10.00	12.00	10.00	12.00	10.00	12.00	10.00	12.00
MEAN RECOVERY	7.33	7.83	6.75	7.72	5.88	7.71	6.42	7.06	6.07	7.52	6.81	6.78
ACCURACY AS % REL ERROR	-26.66	-34.78	-32.50	-35.66	-41.18	-35.74	-35.78	-41.14	-39.28	-37.32	-31.94	-43.53
OVERALL STD DEV (S)	2.66	2.59	2.39	2.76	2.13	2.34	1.85	2.25	1.90	1.98	1.83	1.85
OVERALL REL STD DEV, %	36.29	33.07	35.36	35.78	36.21	30.33	28.86	31.82	31.22	26.29	26.90	27.28
SINGLE STD DEV, (SR)	1.31		1.75		1.00		1.47		.99		1.43	
ANALYST REL DEV, %	17.22		24.25		14.73		21.82		14.58		21.02	
HIGH YOUDEN PAIR	2	4	2	4	2	4	2	4	2	4	2	4
NUMBER OF DATA POINTS	14	14	14	13	16	16	15	16	14	13	15	15
TRUE VALUE UG/L	55.00	45.00	55.00	45.00	55.00	45.00	55.00	45.00	55.00	45.00	55.00	45.00
MEAN RECOVERY	35.15	28.31	35.34	27.87	31.17	27.39	38.00	29.59	31.59	25.47	36.49	28.69
ACCURACY AS % REL ERROR	-36.09	-37.08	-35.75	-38.07	-43.32	-39.14	-30.90	-34.25	-42.56	-43.39	-33.65	-36.24
OVERALL STD DEV (S)	14.05	9.72	11.68	10.16	10.78	12.21	8.66	8.50	10.47	10.24	13.19	8.11
OVERALL REL STD DEV, %	39.96	34.32	33.06	36.47	34.58	44.59	22.79	28.73	33.16	40.18	36.14	28.27
SINGLE STD DEV, (SR)	7.24		8.38		11.25		5.73		5.41		7.28	
ANALYST REL DEV, %	22.82		26.51		38.41		16.94		18.96		22.33	

WATER LEGEND

1 - DISTILLED WATER
2 - TAP WATER
3 - SURFACE WATER
4 - WASTEWATER (C-44)
5 - WASTEWATER (C-45)
6 - WASTEWATER (C-46)

TABLE 9. STATISTICAL SUMMARY FOR 2,6-DINITROTOLUENE ANALYSES BY WATER TYPE

	WATER 1		WATER 2		WATER 3		WATER 4		WATER 5		WATER 6	
LOW YOUDEN PAIR	3	5	3	5	3	5	3	5	3	5	3	5
NUMBER OF DATA POINTS	14	14	17	15	16	15	15	14	14	15	15	16
TRUE VALUE UG/L	1.40	1.00	1.40	1.00	1.40	1.00	1.40	1.00	1.40	1.00	1.40	1.00
MEAN RECOVERY	1.03	.89	1.14	.76	1.17	.90	1.09	.87	1.06	.75	1.03	.81
ACCURACY AS % REL ERROR	-26.56	-11.01	-18.39	-24.07	-16.37	-9.62	-22.33	-13.13	-24.47	-25.27	-26.70	-19.16
OVERALL STD DEV (S)	.41	.29	.32	.25	.42	.36	.27	.23	.36	.39	.35	.27
OVERALL REL STD DEV, %	40.28	32.23	28.29	32.53	36.11	39.99	24.80	26.93	34.02	52.85	34.46	33.34
SINGLE STD DEV, (SR)	.24		.21		.26		.18		.23		.18	
ANALYST REL DEV, %	24.98		22.02		25.41		17.99		25.28		19.24	
MEDIUM YOUDEN PAIR	1	6	1	6	1	6	1	6	1	6	1	6
NUMBER OF DATA POINTS	15	15	16	16	15	15	15	14	15	15	16	15
TRUE VALUE UG/L	10.00	12.00	10.00	12.00	10.00	12.00	10.00	12.00	10.00	12.00	10.00	12.00
MEAN RECOVERY	7.54	8.64	6.83	8.84	6.47	8.53	6.75	8.34	7.46	9.29	7.40	8.10
ACCURACY AS % REL ERROR	-24.57	-27.98	-31.74	-26.31	-35.29	-28.88	-32.47	-30.52	-25.41	-22.62	-25.98	-32.51
OVERALL STD DEV (S)	2.66	3.08	2.57	3.21	2.17	2.39	2.03	2.34	1.93	2.28	2.06	2.64
OVERALL REL STD DEV, %	35.29	35.60	37.58	36.27	33.56	27.97	30.10	28.12	25.81	24.61	27.80	32.57
SINGLE STD DEV, (SR)	1.18		1.67		.92		.99		.69		1.48	
ANALYST REL DEV, %	14.56		21.29		12.27		13.15		8.30		19.03	
HIGH YOUDEN PAIR	2	4	2	4	2	4	2	4	2	4	2	4
NUMBER OF DATA POINTS	15	15	16	15	16	16	14	15	15	14	16	16
TRUE VALUE UG/L	60.00	50.00	60.00	50.00	60.00	50.00	60.00	50.00	60.00	50.00	60.00	50.00
MEAN RECOVERY	35.28	31.77	37.18	31.68	35.76	31.13	40.72	34.18	35.47	31.57	39.23	33.37
ACCURACY AS % REL ERROR	-41.20	-36.45	-38.03	-36.65	-40.39	-37.74	-32.13	-31.63	-40.88	-36.86	-34.62	-33.26
OVERALL STD DEV (S)	14.22	10.36	13.82	12.13	13.28	12.46	7.77	8.60	8.79	10.31	13.58	7.98
OVERALL REL STD DEV, %	40.30	32.59	37.16	38.31	37.13	40.03	19.09	25.16	24.79	32.67	34.63	23.91
SINGLE STD DEV, (SR)	7.82		8.70		11.52		6.08		6.26		7.49	
ANALYST REL DEV, %	23.34		25.26		34.45		16.24		18.66		20.64	

WATER LEGEND

1 - DISTILLED WATER
2 - TAP WATER
3 - SURFACE WATER
4 - WASTEWATER (C-44)
5 - WASTEWATER (C-45)
6 - WASTEWATER (C-46)

TABLE 10. REGRESSION EQUATIONS FOR ACCURACY AND PRECISION OF METHOD 609 BY COMPOUND AND WATER TYPE

WATER TYPE	NITROBENZENE	ISOPHORONE	2,6-DINITROTOLUENE	2,4-DINITROTOLUENE
	(25-425 µg/L)[a]	(25-475 µg/L)[a]	(1-60 µg/L)[a]	(1-55 µg/L)[a]
DISTILLED WATER				
SINGLE-ANALYST PRECISION	SR = 0.25X + 2.53	SR = 0.28X + 2.77	SR = 0.19X + 0.06	SR = 0.20X + 0.08
OVERALL PRECISION	S = 0.37X - 0.78	S = 0.46X + 0.31	S = 0.36X - 0.00	S = 0.37X - 0.07
ACCURACY	X = 0.60C + 2.00	X = 0.49C + 2.93	X = 0.66C + 0.20	X = 0.65C + 0.22
TAP WATER				
SINGLE-ANALYST PRECISION	SR = 0.30X + 1.63	SR = 0.45X - 3.07	SR = 0.23X - 0.02	SR = 0.25X + 0.03
OVERALL PRECISION	S = 0.45X - 1.24	S = 0.60X - 3.27	S = 0.37X - 0.06	S = 0.35X - 0.06
ACCURACY	X = 0.71C - 0.34	X = 0.66C + 1.76	X = 0.66C + 0.14	X = 0.65C + 0.17
SURFACE WATER				
SINGLE-ANALYST PRECISION	SR = 0.37X - 2.20	SR = 0.37X + 1.67	SR = 0.24X + 0.00	SR = 0.27X + 0.08
OVERALL PRECISION	S = 0.43X - 2.87	S = 0.46X - 0.06	S = 0.34X + 0.03	S = 0.34X + 0.21
ACCURACY	X = 0.69C - 0.99	X = 0.59C - 0.03	X = 0.63C + 0.28	X = 0.59C + 0.25
WASTEWATER (C-44)				
SINGLE-ANALYST PRECISION	SR = 0.18X + 2.10	SR = 0.27X + 2.06	SR = 0.15X + 0.03	SR = 0.18X + 0.09
OVERALL PRECISION	S = 0.26X + 0,54	S = 0.33X + 3.75	S = 0.25X + 0.01	S = 0.28X + 0.04
ACCURACY	X = 0.68C - 0.38	X = 0.67C - 1.23	X = 0.67C + 0.18	X = 0.64C + 0.21
WASTEWATER (C-45)				
SINGLE-ANALYST PRECISION	SR = 0.20X + 3.10	SR = 0.22X + 7.15	SR = 0.13X + 0.11	SR = 0.16X + 0.09
OVERALL PRECISION	S = 0.38X - 0.58	S = 0.52X - 1.16	S = 0.25X + 0.17	S = 0.32X + 0.09
ACCURACY	X = 0.61C + 2.25	X = 0.62C + 1.87	X = 0.68C + 0.09	X = 0.60C + 0.01
WASTEWATER (C-46)				
SINGLE-ANALYST PRECISION	SR = 0.16X + 2.48	SR = 0.26X + 6.86	SR = 0.20X - 0.01	SR = 0.22X - 0.05
OVERALL PRECISION	S = 0.26X + 1.88	S = 0.54X + 1.64	S = 0.29X + 0.04	S = 0.29X + 0.03
ACCURACY	X = 0.75C - 1.15	X = 0.62C +12.63	X = 0.67C + 0.12	X = 0.64C + 0.16

(a) Concentration range of compound for which regression equations are generally applicable.

X = MEAN RECOVERY

C = TRUE VALUE FOR THE CONCENTRATION

analyses are summarized in Table 11. The detailed analysis of variance tables supporting these results are presented in Appendix D.

TABLE 11. SUMMARY OF THE TESTS FOR THE DIFFERENCES ACROSS WATER TYPES

Compound	Observed F-Value	P[F > F OBS]	F-Test Statistically Significant at the 5% Level?	Significance Effect Established by the 95% Confidence Intervals?	Practical Significance Established
Nitrobenzene	1.44	0.16	NO	NO	NO
Isophorone	1.70	0.08	NO	NO	No
2,4-Dinitrotoluene	2.48	0.01	Yes	Yes	NO
2,6-Dinitrotoluene	1.47	0.15	NO	No	NO

In all cases except for 2,4-dinitrotoluene, there was no evidence of a statistically significant effect on accuracy or precision due to water type. In the case of 2,4-dinitrotoluene, a statistically significant effect was established since $P[F > F\ OBS] \leq 0.05$. The simultaneous confidence intervals for $\ell n\ \beta_j - \ell n\ \beta_1$ and $\gamma_j - \gamma_1$ all included zero except for the fifth wastewater, C-45. In that case the confidence interval for $\gamma_5 - \gamma_1$ included zero, but the confidence interval for $\ell n\ \beta_5 - \ell n\ \beta_1$ failed to cover zero. This indicated that the statistically significant effect was associated with the C-45 wastewater.

In order to determine if the effect was of practical importance, Equations (15) and (16) were used to relate the mean recovery and precision of the 2,4-dinitrotoluene data in wastewater C-45 to the mean recovery and precision of the 2,4-dinitrotoluene data in distilled water.

The point estimate for $\ell n\ \beta_5 - \ell n\ \beta_1$ was -0.34; the confidence interval for this difference was (-0.609, -0.0650). Therefore, the point estimate for β_5/β_1 is given by (0.545, 0.937). By combining these point estimates with Equations (15) and (16), it can be stated that the mean recovery for 2,4-dinitrotoluene in wastewater C-45 is between 54 percent and 94 percent of the recovery in distilled water. Similarly, the standard deviation of the 2,4-dinitrotoluene measurements in wastewater C-45 is between 54 percent and 94 percent of the standard deviation of the measurements in distilled water.

Based on these results and a comparison of the basic summary statistics for 2,4-dinitrotoluene in Table 8, it was determined that an effect of practical importance due to wastewater C-45 has not been established.

METHOD PERFORMANCE

The specific steps having a primary impact on method performance include:

(a) Solvent extraction of the water sample.

(b) Activation of the Florisil adsorbent and subsequent preparation of the cleanup column.

(c) Concentration and exchange of the solvent extracts and Florisil fractions.

(d) Operation of the GC/FID and GC/ECD system.

Solvent Extraction

The primary problem associated with the solvent extraction step is the formation of emulsions which can lead to reduced recovery for the four Category 4 compounds. Several laboratories reported the formation of emulsions for the wastewater samples. In most cases, simply letting the layer stand for 10-15 minutes or gentle stirring with a glass rod resulted in dissociation of the emulsion. If formation of emulsions is a major factor in determining method performance, one would expect to observe reduced analyte recoveries for the wastewater samples, but not for the drinking water samples. However, recoveries were not significantly different between distilled water and the three wastewater samples as shown in Table 10. Therefore, emulsion formation did not appear to be a significant factor in determining method performance for this study.

Florisil Adsorbent and Column Cleanup

Proper activation of the Florisil adsorbent and careful performance of the subsequent column preparation and cleanup steps were found to be important factors during the method development process at Battelle. Incomplete activation of the adsorbent can lead to earlier elution (loss) of nitrobenzene, in particular. Consequently, if such a problem was a major

factor in the data set one would expect to observe reduced recovery for nitrobenzene. However, an examination of Table 10 reveals equivalent or slightly higher average recovery for nitrobenzene as compared to the dinitrotoluenes. An examination of data from individual laboratories did not indicate any evidence of selective loss of nitrobenzene. Consequently, one can conclude that Florisil activation was not a major source of error in the data.

Concentration and Exchange of Solvent Extract

Volatilization during the extraction, concentration, and solvent exchange steps can be a significant source of error in methods of this type. In this case, nitrobenzene and isophorone would be lost to a greater extent than the less volatile dinitrotoluenes. Again, Table 10 does not indicate such a trend, implying volatilization losses were not a major source of error in the data set.

Another potential source of error in the extraction, concentration, and solvent exchange steps is partial loss of the extract by bumping of solutions during evaporation of solvents. This phenomenon was reported to be a problem by nearly two-thirds of the laboratories; careful operator attention was required to avoid the problem. This source of error gave reduced recovery for all compounds; therefore, Table 10 is consistent with this potential source of error.

Because of the large number of laboratories reporting bumping, this source of error may in fact be highly significant, and users of the method should pay careful attention to this section of the method. In general a uniform distribution and rate of heating and the use of fresh boiling chips during the solvent exchange step are critical factors in reducing the occurrence of bumping. Many laboratories found it to be advantageous to conduct the final concentration step (from 10 mL to 1 mL) on one sample at a time, with gentle agitation to avoid bumping.

GC/FID and GC/ECD Systems

The final step of the method, GC determination, is also a potential source of error. Improper calibration can arise due to the inaccurate

preparation of standard solutions or the use of calibration concentrations of analyte greatly different from the analyte concentrations in the sample (i.e. response is nonlinear). Such errors would be expected to be random, from laboratory to laboratory, thereby increasing the overall standard deviation but not the single-analyst relative standard deviation. Similar errors would be observed for the various water types. The data obtained (Table 10) do not rule out the possibility of the GC determination as a source of error. However, review of the individual laboratory data did not reveal any obvious calibration errors. Moreover, the data in Table 10 indicate that single analyst standard deviation is a major portion of the overall standard deviation, thus minimizing the importance of GC calibration errors.

GENERAL DISCUSSION

Inspection of the summary statistics and raw data for this study revealed very few trends which could be used to pinpoint specific deficiencies in the method. Losses of all four analytes due to bumping during the concentration step was the only probable source of error identified as previously discussed. The data presented in Table 10 reveal no specific differences in recovery between compounds or between water types, except that isophorone gave a somewhat lower recovery from distilled water then the other five water types. The reason(s) for this result are not clear, since previous studies at Battelle (8) did not show such a trend. One possible explanation is that distilled water was the first matrix analyzed by all laboratories. Possibly, this learning-curve effect is responsible for the improved recoveries for the other sample types, although such an effect would be expected to occur for all four analytes, not just isophorone.

An important conclusion to be drawn from the data set is that if a laboratory performs well with the method using distilled water, it should be able to obtain similar results with surface waters and industrial wastewater, provided the level of interferences do not overwhelm the components of interest. However, it is important to recognize that several laboratories were unable to achieve good results--good results are defined as comparable to the Battelle single laboratory data (8). A major contributing factor was the experience of the laboratory in applying the method--in other words,

better data will be obtained as a laboratory gains experience with the method. This learning-curve is a factor in performing any organic analytical method, and its duration will depend on the skill and experience level of both the operator and the laboratory. Very little evidence of a learning curve effect is evident in the data set, isophorone being a possible exception as discussed above. However, most laboratories had only a few weeks experience with the method prior to beginning the study. This period is probably not sufficient to ascertain whether a learning-curve effect exists.

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APPENDIX A

NITROAROMATICS AND ISOPHORONE

METHOD 609

1. Scope and Application

1.1 This method covers the determination of certain nitroaromatics and isophorone. The following parameters may be determined by this method:

Parameter	STORET No.
Isophorone	34408
Nitrobenzene	34447
2,4-Dinitrotoluene	34611
2,6-Dinitrotoluene	34626

1.2 This method is applicable to the determination of these compounds in municipal and industrial discharges. It is designed to be used to meet the monitoring requirements of the National Pollutant Discharge Elimination system (NPDES). As such, it presupposes a high expectation of finding the specific compounds of interest. If the user is attempting to screen samples for any or all of the compounds above, he must develop independent protocols for the verification of identity.

1.3 The sensitivity of this method is usually dependent upon the level of interferences rather than instrumental limitations. The limits of detection listed in Table A-1 represent sensitivities that can be achieved in wastewaters in the absence of interferences.

1.4 This method is recommended for use only by experienced residue analysts or under the close supervision of such qualified persons.

2. Summary of Method

2.1 A 1-liter sample of wastewater is extracted with methylene chloride using separatory funnel techniques. The extract is dried and

TABLE A-1. GAS CHROMATOGRAPHY OF NITROAROMATICS AND ISOPHORONE

Compound	Retention Time(min.)		Detection Limit (µg/L)	
	Column 1	Column 2	EC	FID
Isophorone	4.49	5.72	-	5
Nitrobenzene	3.31	4.31	-	5
2,4-Dinitrotoluene	5.35	6.54	0.06	-
2,6-Dinitrotoluene	3.52	4.75	0.06	-

Column 1 conditions: Gas-Chrom Q 80/100 mesh coated with 1.95 percent QF-1/1.5 percent OV-17 packed in a 4' x 1/4" OD glass column. FID analysis for IP and NB requires nitrogen carrier gas at 44 mL/min and 85°C column temperature. EC analysis for the DNTs requires 10 percent methane/90 percent argon carrier gas at 44 mL/min flow rate and 145°C column temperature.

Column 2 conditions: Gas-Chrom Q 80/100 mesh coated with 3 percent OV-101 packed in a 10' x 1/4" OD glass column. FID analysis of IP and NB requires nitrogen carrier gas at 44 mL/min flow rate and 100°C column temperature. EC analysis for the DNTs requires 10 percent methane/90 percent argon carrier gas at 44 mL/min flow rate and 150°C column temperature.

Detection limit is calculated from the minimum detectable GC response being equal to five times the GC background noise, assuming a 10 mL final volume of the 1 liter sample extract, and assuming a GC injection of 5 microliters.

exchanged to toluene while being concentrated to 1.0 mL. Isophorone and nitrobenzene are measured by flame ionization gas chromatography. The dinitrotoluenes are measured by electron capture GC.

2.2 If interferences are encountered, the method provides a general purpose cleanup procedure to aid the analyst in their elimination.

3. Interferences

3.1 Solvents, reagents, glassware, and other sample processing hardware may yield discrete artifacts and/or elevated baselines causing misinterpretation of gas chromatograms. All of these materials must be demonstrated to be free from interferences under the conditions of the analysis by running method blanks. Specific selection of reagents and purification of solvents by distillation in all-glass systems may be required.

3.2 Interferences coextracted from the samples will vary considerably from source to source, depending upon the diversity of the industrial complex or municipality being sampled. While general clean-up techniques are provided as part of this method, unique samples may require additional cleanup approaches to achieve the sensitivities stated in Table A-1.

4. Apparatus and Materials

4.1 Sampling equipment, for discrete or composite sampling.

4.1.1 Grab sample bottle - amber glass, 1-liter or 1-quart volume. French or Boston Round design is recommended. The container must be washed and solvent rinsed before use to minimize interferences.

4.1.2 Bottle caps - Threaded to screw on to the sample bottles. Caps must be lined with Teflon. Foil may be substituted if sample is not corrosive.

4.1.3 Compositing equipment - Automatic or manual compositing system. Must incorporate glass sample containers for the collection of a minimum of 250 mL. Sample containers must be kept refrigerated during sampling. No tygon or rubber tubing may be used in the system.

4.2 Separatory funnel - 200 mL, with Teflon stopcock.

4.3 Drying column - 20 mm ID pyrex chromatographic column with coarse frit.

4.4 Kuderna-Danish (K-D) Apparatus

4.4.1 Concentrator tube - 10 mL, graduated (Kontes K-570050-1025 or equivalent). Calibration must be checked. Ground glass stopper (size 19/22 joint) is used to prevent evaporation of extracts.

4.4.2 Evaporative flask - 500 mL (Kontes K-57001-0500 or equivalent). Attach to concentrator tube with springs. (Kontes K-662750-0012).

4.4.3 Snyder column - three-ball macro (Kontes K503000-0121 or equivalent).

4.4.4 Snyder column - two-ball micro (Kontes K-569001-0219 or equivalent).

4.4.5 Boiling chips - solvent extracted, approximately 10/40 mesh.

4.5 Water bath - Heated, with concentric ring cover, capable of temperature control (± 2°C). The bath should be used in a hood.

4.6 Gas chromatograph - Analytical system complete with gas chromatograph suitable for on-column injection and all required accessories including both electron capture and flame ionization detectors, column supplies, recorder, gases, syringes. A data system for measuring peak areas is recommended.

4.7 Chromatography column - 400 mm long x 10 mm ID, with coarse fritted plate on bottom and Teflon stopcock.

5. Reagents

5.1 Preservatives:

5.1.1 Sodium hydroxide - (ACS) 10 N in distilled water.

5.1.2 Sulfuric acid (1+1) - (ACS) Mix equal volumes of conc. H_2SO_4 with distilled water.

5.2 Methylene chloride - Pesticide quality or equivalent.

5.3 Sodium sulfate - (ACS) Granular, anhydrous (purified by heating at 400°C for 4 hrs. in a shallow tray).

5.4 Stock standards - Prepare stock standard solutions at a concentration of 1.00 µg/µL by dissolving 0.100 grams of assayed

reference material in pesticide quality isooctane or other appropriate solvent and diluting to volume in a 100 mL ground glass stoppered volumetric flask. The stock solution is transferred to ground glass stoppered reagent bottles, stored in a refrigerator, and checked frequently for signs of degradation or evaporation, especially just prior to preparing working standards from them.

5.5 Acetone, Hexane, Methanol - pesticide quality or equivalent.

5.6 Florisil - PR grade (60/100 mesh); purchase activated at 1250°F and store in glass containers with glass stoppers or foil-lined screw caps. Before use, activate each batch overnight at 200°C in glass containers loosely covered with foil.

6. Calibration

6.1 Prepare calibration standards that contain the compounds of interest, either singly or mixed together. The standards should be prepared at concentrations covering two or more orders of magnitude that will completely bracket the working range of the chromatographic system. If the sensitivity of the detection system can be calculated from Table A-1 as 100 µg/L, 50 µg/L, 100 µg/L, 500 µg/L, etc. so that injections of 1-5 µL of each calibration standard will define the linearity of the detector in the working range.

6.2 Assemble the necessary gas chromatographic apparatus and establish operating parameters equivalent to those indicated in Table A-1. By injecting calibration standards, establish the sensitivity limit of the detector and the linear range of the analytical system for each compound.

6.3 Before using any cleanup procedure, the analyst must process a series of calibration standards through the procedure to validate elution patterns and the absence of interferences from the reagents.

7. Quality Control

7.1 Before processing any samples, the analyst should demonstrate through the analysis of a distilled water method blank, that all glassware and reagents are interference-free. Each time a set of samples is extracted or there is a change in reagents, a method

blank should be processed as a safeguard against chronic laboratory contamination.

7.2 Standard quality assurance practices should be used with this method. Field replicates should be collected to validate the precision of the sampling technique. Laboratory replicates should be analyzed to validate the precision of the analysis. Fortified samples should be analyzed to validate the accuracy of the analysis. Where doubt exists over the identification of a peak on the chromatogram, confirmatory techniques such as mass spectroscopy should be used.

8. Sample Collection, Preservation, and Handling

8.1 Grab samples must be collected in glass containers. Conventional sampling practices should be followed, except that the bottle must not be prewashed with sample before collection. Composite samples should be collected in refrigerated glass containers in accordance with the requirements of the program. Automatic sampling equipment must be free of tygon and other potential sources of contamination.

8.2 The samples must be iced or refrigerated from the time of collection until extraction. Chemical preservatives should not be used in the field unless more than 24 hours will elapse before delivery to the laboratory. If the samples will not be extracted within 48 hours of collection, the sample should be adjusted to a pH range of 6.0-8.0 with sodium hydroxide or sulfuric acid.

8.3 All samples must be extracted within 7 days and completely analyzed within 30 days of collection.

9. Sample Extraction

9.1 Mark the water meniscus on the side of the sample bottle for later determination of sample volume. Pour the entire sample into a two-liter separatory funnel. Check the pH of the sample with wide-range pH paper and adjust to within the range of 5-9 with sodium hydroxide or sulfuric acid.

9.2 Add 60 mL methylene chloride to the sample bottle, seal, and shake 30 seconds to rinse the inner walls. Transfer the solvent into the separatory funnel, and extract the sample by shaking the funnel for two minutes with periodic venting to release vapor pressure. Allow

the organic layer to separate from the water phase for a minimum of ten minutes. If the emulsion interface between layers is more than one-third the size of the solvent layer, the analyst must employ mechanical techniques to complete the phase separation. The optimum technique depends upon the sample, but may include stirring, filtration of the emulsion through glass wool, or centrifugation. Collect the methylene chloride extract in a 250-mL Erlenmeyer flask.

9.3 Add a second 60-mL volume of methylene chloride to the sample bottle and complete the extraction procedure a second time, combining the extracts in the Erlenmeyer flask.

9.4 Perform a third extraction in the same manner. Pour the combined extract through a drying column containing 3-4 inches of anhydrous sodium sulfate, and collect it in a 500-mL Kuderna-Danish (K-D) flask equipped with a 10 mL concentrator tube. Rinse the Erlenmeyer flask and column with 20-30 mL methylene chloride to complete the quantitative transfer.

9.5 Add 1-2 clean boiling chips to the flask and attach a three-ball Snyder column. Prewet the Snyder column by adding about 1 mL methylene chloride to the top. Place the K-D apparatus on a hot water bath (60-65°C) so that the concentrator tube is partially immersed in the hot water, and the entire lower rounded surface of the flask is bathed in vapor. Adjust the vertical position of the apparatus and the water temperature as required to complete the concentration in 15-20 minutes. At the proper rate of distillation the balls of the column will actively chatter but the chambers will not flood. When the apparent volume of liquid reaches 1 mL, remove the K-D apparatus and allow it to drain for at least 10 minutes while cooling. Remove the Snyder column and rinse the flask and its lower joint into the concentrator tube with 1-2 mL of methylene chloride. A 5 mL syringe is recommended for this operation. Add 1.0 mL hexane to the concentrator tube, and a clean boiling chip. Attach a two-ball micro-Snyder column. Prewet the micro-Snyder column by adding about 0.5 mL of methylene chloride to the top. Place this micro-K-D apparatus on a water bath (60-65°C) so that the

concentrator tube is partially immersed in the hot water. Adjust the vertical position of the apparatus and water temperature as required to complete the concentration in 10 to 50 minutes. At the proper rate of distillation the balls will actively chatter but the chambers will not flood. When the apparent volume of liquid reaches 0.5 mL, remove the K-D apparatus and allow it to drain for at least 10 minutes while cooling. Remove the micro-Snyder column and rinse its lower joint into the concentrator tube with a small volume of hexane. Adjust the final volume to 1.0 mL and stopper the concentrator tube and store refrigerated if further processing will not be performed immediately. Unless the sample is known to require cleanup, proceed with gas chromatographic analysis.

9.7 Determine the original sample volume by refilling the sample bottle to the mark and transferring the liquid to a 1000 mL graduated cylinder. Record the sample volume to the nearest 5 mL.

10. Cleanup and Separation

10.1 Prepare a slurry of 10g of activated Florisil in 10% methylene chloride in hexane (V/V). Use it to pack a 10 mm ID chromatography column, gently tapping the column to settle the Florisil. Add 1 cm anhydrous sodium sulfate to the top of the Florisil.

10.1.1 Just prior to exposure of the sodium sulfate layer to the air transfer the 1 mL sample extract onto the column using an additional 2 mL of hexane to complete the transfer.

10.1.2 Just prior to exposure of the sodium sulfate layer to the air, add 30 mL 10% methylene chloride in hexane and continue the elution of the column. Elution of the column should be at a rate of about 2 mL per minute. Discard the eluate from this fraction.

10.1.3 Next elute the column with 30 mL of 10% acetone/90% methylene chloride (V/V) into a 500 mL K-D flask equipped with a 10 mL concentrator tube. Concentrate the collected fraction by the K-D technique prescribed in 9.5 and 9.6, including the solvent exchange to 1 mL hexane. This fraction should contain the nitroaromatics and isophorone.

10.1.4 Analyze by gas chromatography.

11. Gas Chromatography

11.1 Isophorone and nitrobenzene are analyzed by injection of a portion of the extract into a gas chromatograph with a flame ionization detector. The dinitrotoluenes are analyzed by a separate injection into an electron capture gas chromatograph. Table A-1 summarizes some recommended gas chromatographic column materials and operating conditions for the instruments. Included in this table are estimated retention times and sensitivities that should be achieved by this method. Examples of the separations achieved by the primary column are shown in Figures A-1 and A-2. Calibrate the system daily with a minimum of three injections of calibration standards.

11.2 Inject 2-5 µL of the sample extract using the solvent-flush technique. Smaller (1.0 µL) volumes can be injected if automatic devices are employed. Record the volume injected to the nearest 0.05 µL, and the resulting peak size, in area units.

11.3 If the peak area exceeds the linear range of the system, dilute the extract and reanalyze.

11.4 If the peak area measurement is prevented by the presence of interferences, further cleanup is required.

12. Calculations

12.1 Determine the concentration of individual compounds according to the formula:

$$\text{Concentration, } \mu g/L = \frac{(A)\ (B)\ (V_t)}{(V_i)\ \ (V_s)}$$

where A = Calibration factor for chromatographic system, in namograms material per unit area

B = Peak size in injection of sample extract, in area units

V_i = Volume of extract injected (µL)

V_t = Volume of total extract (µL)

V_s = Volume of water extracted (mL).

12.2 Report results in micrograms per liter without correction for recovery data. When duplicate and spiked samples are analyzed, all data obtained should be reported.

BIBLIOGRAPHY

"Development and Application of Test Procedures for Specific Organic Toxic Substances in Wastewaters. Category 4-Nitroaromatics and Isophorone," Report for EPA Contract No. 68-03-2624 (In preparation).

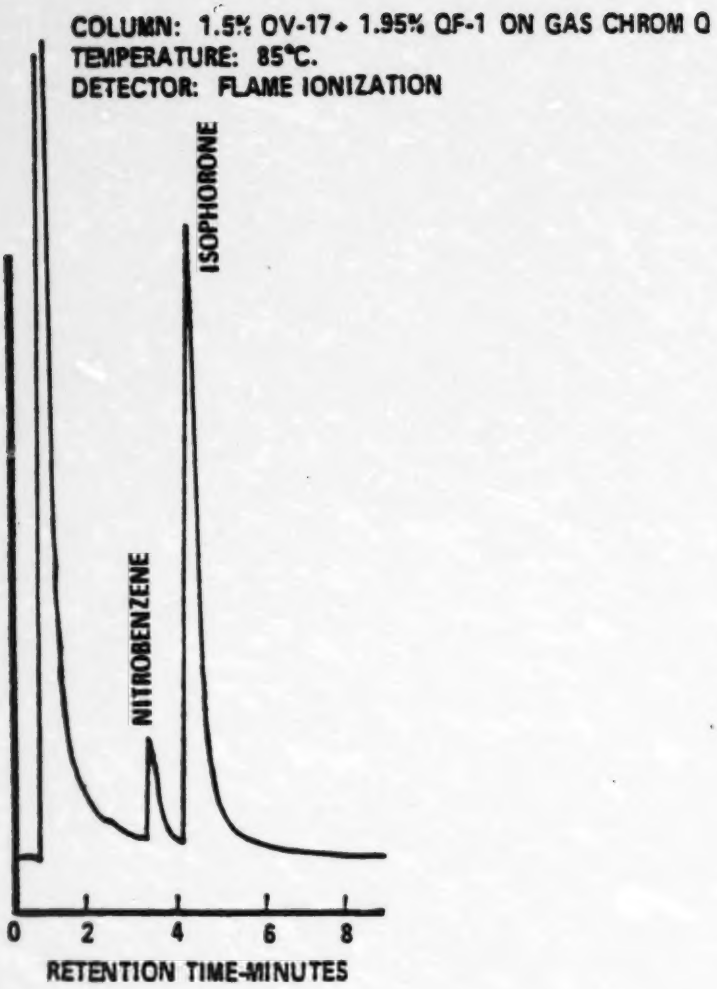

Figure A-1. Gas Chromatogram of Nitrobenzene and Isophorone

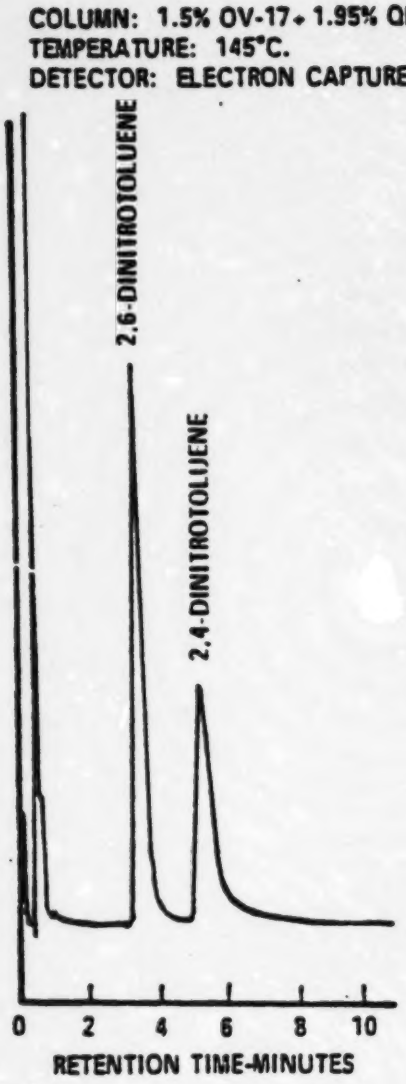

Figure A-2. Gas Chromatogram of Dinitrotoluenes

APPENDIX B

MODIFICATIONS TO METHOD 609 AND INSTRUCTIONS TO ANALYST

Summarized below are: 1) modifications to Method 609 discussed at the prestudy conference July 17, 1979 and subsequently approved by EPA, and 2) instructions sent to the analyst prior to the start of the method study.

MODIFICATIONS TO METHOD 609

a) Hexane (pesticide quality or equivalent) should be added to the list of reagents required.

b) Paragraph 5.6 - The last sentence should read "Before use, activate each batch overnight at 200°C in glass containers loosely covered with foil".

c) Paragraph 9.6 - The first phrase of the first sentence should read "Add 1.0 mL hexane to the concentration tube ".....

d) Paragraph 10.1 - The first sentence should read "Prepare a slurry of 10 grams of Florisil in 90 percent hexane/10 percent methylene chloride".

e) Paragraph 10.1.3 - The first sentence should read "Just prior to exposure of the sodium sulfate layer to the air, add 30 mL of 90 percent hexane/10 percent methylene chloride and continue the elution of the column.

f) Paragraph 11.1 - a 6 ft x 2 mm ID glass column and a 6 ft x 4 mm ID glass column each packed with Gas-Chrom Q 80/100 mesh coated with 1.95 percent QF-1/1.5 percent OV-17 are to be used in this work. The 2 mm column is to be used for the FID analysis of isophorone and nitrobenzene and the 4 mm column is to be used for the ECD analysis of the dinitrotoluenes. Carrier gas flow rates may be adjusted as necessary to obtain good separation.

INSTRUCTIONS TO THE ANALYST

In the application of Method 609, the performance of the chromatographic clean-up step must be carefully controlled. All solvents used in the clean-up step, as well as the sample itself, must be completely dry. When activating the florisil it is important to only loosely place foil over the jar, since a tightly covered jar will prevent proper activation. If the florisil is not properly activated the nitroaromatics will carry over in the first (hexane/methylene chloride) fraction.

In performing the GC analysis a plug of one microliter of toluene should be drawn into the syringe prior to drawing in the desired amount of sample.

Performance of the GC instrumentation is critical. Both the ECD and FID sensitivity should be checked daily. The following amounts of compound on column will give approximately 1/2 scale peaks with approximately 0.5 percent full scale noise:

Nitrobenzene - 100 ng
Isophorone - 100 ng
2,6-Dinitrotoluene - 1 ng
2,4-Dinitrotoluene - 1 ng

For Nitrobenzene and Isophorone the amount of solvent tailing will determine sensitivity. Therefore it is important that the solvent tail be minimized by eliminating inefficiencies in the injection port (e.g. unswept "dead" volume).

All wastewaters must be analyzed using the specified procedures, including clean-up. Adsorbent materials used in the column clean-up steps must be activated in each laboratory. Each eluate fraction from the clean-up of the trail samples should be saved, and, if low recoveries are observed in the proper fraction, the previous fractions should be analyzed to determine if breakthrough has occurred.

APPENDIX C

TABLE C-1. RAW DATA FOR NITROBENZENE ANALYSIS BY WATER TYPE

	WATER 1		WATER 2		WATER 3		WATER 4		WATER 5		WATER 6	
LOW YOUDEN PAIR	3	5	3	5	3	5	3	5	3	5	3	5
TRUE VALUE UG/L	35.00	25.00	35.00	25.00	35.00	25.00	35.00	25.00	35.00	25.00	35.00	25.00
LABORATORY NUMBER												
101	21.00	20.00	34.00	20.00	37.00	18.00	30.00	25.00	28.00	16.00	32.00	14.00
102	7.48	12.40	31.20	7.39	20.60	14.20	30.30	8.31	19.80	8.97	32.20	18.80
103	9.00*	8.00*	6.00	25.00	25.00*	7.00*	*	13.00*	7.00	25.00	11.00*	10.00*
104	28.00	15.00	23.00	19.00	24.00	17.00	23.00	13.00	15.00	13.00	25.00	16.00
105	28.00	14.00	31.00	18.00	22.00	14.00	21.00	19.00	14.00	17.00	18.00	7.00
106	13.10	19.60	2.42	1.60	28.60	22.80	30.20	16.30	27.00	2.42	21.60	9.79
107	46.10*	23.80*	33.10	11.60	35.50	15.80	30.40	19.00	41.50	21.00	38.20	27.60
108	10.80*	5.60*	11.30*	3.06*	0.00*	0.00*	2.48*	2.34*	4.15*	2.20*	0.61*	1.60*
109	9.73	0.00*	23.00	13.39	12.89	13.11	21.43	12.97	22.32	17.39	21.77	17.60
110	23.60	16.80	31.60	20.80	19.00	15.80	10.10	10.60	26.20	19.50	48.30	23.90
111	27.00	22.00	30.00	51.00*	26.00	40.00*	30.00	39.00*	17.00	22.00	18.00	24.00
112	16.86	18.08	29.97	*	24.80	17.50	20.40	18.60	25.10	14.60	*	7.20
113	22.00	11.00	23.00	21.00	35.00*	17.00*	36.00*	19.00*	24.00	19.00	16.00	20.00
114	38.30	23.20	12.60	16.30	18.10	17.70	24.90	20.60	29.40	29.00	19.10	15.80
115	*	18.40	26.70	16.60	25.60	17.60	15.60	26.20	22.20	15.50	24.80	18.80
116	1.58	21.90	31.60	22.60	10.50	10.60	26.40	14.50	0.00*	12.50*	12.10*	6.91*
117	23.20	23.20	48.30	18.80	85.60*	7.60	19.30	14.80	27.60	20.20	44.10*	33.30*
118	28.00	15.00	27.00	19.00	36.00	17.00	28.00	12.00	*	23.00*	29.00	16.00

* = REJECTED

WATER LEGEND

1 - DISTILLED WATER
2 - TAP WATER
3 - SURFACE WATER
4 - WASTEWATER (C-44)
5 - WASTEWATER (C-45)
6 - WASTEWATER (C-46)

APPENDIX C (Continued)

TABLE C-1. RAW DATA FOR NITROBENZENE ANALYSIS BY WATER TYPE

	WATER 1		WATER 2		WATER 3		WATER 4		WATER 5		WATER 6	
MEDIUM YOUDEN PAIR	1	6	1	6	1	6	1	6	1	6	1	6
TRUE VALUE UG/L	210.00	175.00	210.00	175.00	210.00	175.00	210.00	175.00	210.00	175.00	210.00	175.00
LABORATORY NUMBER												
101	130.00	140.00	130.00	140.00	130.00	130.00	150.00	150.00	160.00	170.00	150.00	99.00
102	59.10	103.90	*	139.70	63.10	87.10	134.50	137.60	119.60	116.50	132.50	137.40
103	38.00*	49.00*	55.00	74.00	0.00*	25.00*	42.00*	13.00*	0.00*	42.00	23.00*	52.00*
104	130.00	110.00	79.00 <	1.00*	140.00	150.00	140.00	110.00	150.00	140.00	140.00	96.00
105	161.00	188.00*	157.00	137.00	155.00	155.00	153.00	150.00	112.00	152.00	120.00	163.00
106	188.00	82.20	192.00	135.00	156.00	80.70	144.00	111.00	121.00	82.40	150.00	66.20
107	250.00*	207.00*	256.00	233.00	302.00	207.00	177.00	140.00	0.00*	161.00	195.00	183.00
108	1.09*	0.00*	62.00*	51.50*	11.00*	8.95*	35.40*	11.20*	13.60*	28.50*	26.70*	19.30*
109	126.00	121.00	179.00	132.30	4.16	158.40	162.50	133.70	224.80	166.00	181.90	146.90
110	146.00	90.60	141.00	133.00	147.00	100.00	97.40	104.00	173.00	138.00	159.00	138.00
111	111.00	85.00	60.00	48.00	66.00	131.00	57.00	130.00	56.00	107.00	24.00*	132.00
112	149.60	129.30	143.30	136.50	134.50	117.90	100.40	*	153.80	106.00	151.10	132.50
113	204.00	127.00	227.00	156.00	215.00*	212.00*	176.00*	174.00*	212.00	183.00	109.00	71.00
114	148.00	73.40	101.00	78.30	114.00	60.90	112.00	102.00	131.00	119.00	173.00	94.10
115	124.00	106.00	124.00	93.10	121.00	110.00	145.00	122.00	147.00	120.00	146.00	*
116	18.50	129.00	4.27	96.20	283.00	81.80	337.00*	301.00*	3.69*	30.70*	75.70*	44.20*
117	132.10	114.30	182.80	176.90	277.50	97.40	137.70	79.10	129.10	94.70	185.80*	153.30*
118	194.00	127.00	171.00	143.00	129.00	209.00	276.00*	210.00*	170.00*	166.00*	240.00	220.00

* = REJECTED

WATER LEGEND

1 - DISTILLED WATER
2 - TAP WATER
3 - SURFACE WATER
4 - WASTEWATER (C-44)
5 - WASTEWATER (C-45)
6 - WASTEWATER (C-46)

APPENDIX C (Continued)

TABLE C-1. RAW DATA FOR NITROBENZENE ANALYSIS BY WATER TYPE

	WATER 1		WATER 2		WATER 3		WATER 4		WATER 5		WATER 6	
HIGH YOUDEN PAIR	2	4	2	4	2	4	2	4	2	4	2	4
TRUE VALUE UG/L	425.00	515.00	425.00	515.00	425.00	515.00	425.00	515.00	425.00	515.00	425.00	515.00
LABORATORY NUMBER												
101	340.00	320.00	210.00	390.00	160.00	360.00	310.00	280.00	210.00	380.00	270.00	390.00
102	180.20	203.20	410.50	253.10	246.70	254.50	361.80	441.70	196.50	263.20	248.20	406.80
103	88.00*	25.00*	211.00	205.00	20.00*	13.00*	52.00*	40.00*	32.00	21.00	60.00*	136.00*
104	340.00	390.00	320.00	470.00	330.00	330.00	430.00	400.00	170.00	450.00	270.00	250.00
105	102.00	212.00	274.00	341.00	310.00	228.00	376.00	325.00	220.00	230.00	297.00	213.00
106	300.00	419.00	378.00	366.00	367.00	476.00	259.00	214.00	156.00	192.00	309.00	380.00
107	624.00*	618.00*	543.00	801.00	368.00	702.00	327.00	450.00	0.00*	24.80	391.00	333.00
108	124.00*	78.80*	139.00*	164.00*	27.50*	83.00*	160.00*	30.00*	33.80*	60.00*	21.30*	32.80*
109	373.50	364.60	163.40	521.40	277.30	1.98*	263.20	417.60	387.80	463.90	338.80	441.10
110	244.00	287.00	309.00	341.00	309.00	340.00	342.00	394.00	294.00	360.00	276.00	312.00
111	157.00	238.00	93.00	349.00	219.00	178.00	219.00	256.00	185.00	148.00	217.00	280.00
112	62.05	231.50	286.90	*	287.90	349.40	249.70	369.00	249.80	317.60	297.10	352.20
113	380.00	502.00	426.00	712.00	529.00*	714.00*	504.00*	602.00*	686.00*	528.00*	515.00	713.00*
114	404.00	250.00	314.00	197.00	279.00	183.00	360.00	348.00	369.00	298.00	287.00	385.00
115	267.00	326.00	227.00	*	196.00	256.00	*	361.00	288.00	353.00	430.00	369.00
116	35.70	2.00	56.80	301.00	130.00	29.70	70.60	158.00	141.00*	32.50*	177.00*	250.00*
117	289.30	213.40	383.60	381.90	423.40	426.10	259.60	255.30	300.00	265.40	315.00*	434.60*
118	343.00	416.00	446.00	99.00	330.00	423.00	573.00	400.00	510.00*	440.00*	570.00	502.00

* = REJECTED

WATER LEGEND

1 - DISTILLED WATER
2 - TAP WATER
3 - SURFACE WATER
4 - WASTEWATER (C-44)
5 - WASTEWATER (C-45)
6 - WASTEWATER (C-46)

APPENDIX C (Continued)

TABLE C-2. RAW DATA FOR ISOPHORONE ANALYSIS BY WATER TYPE

	WATER 1		WATER 2		WATER 3		WATER 4		WATER 5		WATER 6	
LOW YOUDEN PAIR	3	5	3	5	3	5	3	5	3	5	3	5
TRUE VALUE UG/L	25.00	35.00	25.00	35.00	25.00	35.00	25.00	35.00	25.00	35.00	25.00	35.00
LABORATORY NUMBER												
101	6.80	22.00	17.00	20.00	17.00	19.00	18.00	38.00	21.00	21.00	43.00	19.00
102	6.28	18.80	19.70	10.90	14.70	21.90	8.90	4.60	13.40	13.90	*	*
103	0.00*	12.00*	0.00*	0.00*	0.00*	15.00*	*	17.00*	25.00	11.00	11.00	14.00
104	18.00	20.00	18.00	29.00	13.00	25.00	13.00	16.00	11.00	19.00	34.00	7.00
105	18.00	22.00 <	5.00*	13.00	7.00	9.00 <	5.00*	11.00*	5.00	54.00	58.00	28.00
106	6.17	23.90	25.40	22.50	21.80	14.30	18.00	25.40	16.50	1.72	5.99	14.90
107	34.90	16.90	23.70	18.20	25.30*	28.10*	0.00*	18.70	32.50	42.00	61.00	94.00*
108	5.51*	6.56*	7.53	2.00	0.00*	2.47*	0.00*	0.00*	0.00*	0.00*	0.00*	18.00
109	8.00	0.00*	15.05	21.79	4.37	24.23	14.09	20.62	17.12	33.22	89.07	63.10*
110	6.96	20.60	28.30	36.90	10.70	22.20	3.25	3.42	11.40	32.60	78.80	46.50
111	22.00	29.00	20.00	19.00	15.00	21.00	24.00	38.00	17.00	17.00	21.00	16.00
112	8.63	28.95	20.82	*	5.23	26.40	7.50	31.50	19.40	27.90	*	35.30
113	22.00	27.00	14.00	34.00	23.00	25.00	22.00	29.00	15.00	30.00	9.90	27.00
114	18.40	21.50	9.25	18.70	10.30	20.60	12.40	29.80	6.78	23.00	-65.50*	6.70*
115	*	48.00*	31.00	39.90	29.10*	43.20*	40.00*	33.90*	28.20*	40.60*	4.00	30.00
116	6.29	32.70	26.90	50.90	22.30	38.90	36.90	29.10	8.11	46.80	1.00	0.00*
117	8.80	23.10	6.40	16.70	26.70	6.20	9.70	13.80	17.10	23.70	39.50	27.60
118	21.00*	28.00*	18.00	33.00	26.00*	31.00*	23.00*	42.00*	*	40.00	18.00	22.00

* = REJECTED

WATER LEGEND

1 - DISTILLED WATER
2 - TAP WATER
3 - SURFACE WATER
4 - WASTEWATER (C-44)
5 - WASTEWATER (C-45)
6 - WASTEWATER (C-46)

APPENDIX C (Continued)

TABLE C-2. RAW DATA FOR ISOPHORONE ANALYSIS BY WATER TYPE

	WATER 1		WATER 2		WATER 3		WATER 4		WATER 5		WATER 6	
MEDIUM YOUDEN PAIR	1	6	1	6	1	6	1	6	1	6	1	6
TRUE VALUE UG/L	150.00	200.00	150.00	200.00	150.00	200.00	150.00	200.00	150.00	200.00	150.00	200.00
LABORATORY NUMBER												
101	32.00	98.00	44.00	130.00	55.00	140.00	75.00	140.00	86.00	160.00	103.00	123.00
102	26.70	64.50	*	174.30	46.20	125.90	77.20	177.30	91.60	145.50	93.50	210.10
103	22.00*	47.00*	30.00	87.00	0.00*	0.00*	19.00*	13.00*	0.00*	33.00	17.00	65.00
104	76.00	110.00	44.00	< 1.00*	86.00	150.00	78.00	130.00	81.00	180.00	89.00	100.00
105	80.00	53.00	81.00	10.00	43.00	149.00	37.00*	47.00*	*	117.00	20.00	226.00
106	112.00	102.00	24.30	135.00	33.80	98.80	84.20	130.00	53.20	104.00	72.60	54.90
107	167.00	274.00*	169.00	307.00	217.00*	302.00*	100.00	142.00	115.00	168.00	153.00	272.00
108	0.00*	0.00*	51.70	92.40	7.29*	35.60*	14.60*	18.30*	8.58*	36.40*	22.80	60.90
109	64.94	104.40	81.00	164.80	13.27	210.20	78.61	152.70	136.20	221.00	131.80	206.40
110	54.70	113.00	56.50	92.80	49.30	72.80	45.40	110.00	92.80	110.00	110.00	130.00
111	60.00	66.00	14.00	56.00	34.00	73.00	40.00	136.00	16.00	72.00	11.00	136.00
112	89.35	164.10	88.06	161.90	79.90	146.60	38.60	*	106.60	149.80	76.10	197.90
113	122.00	150.00	128.00	189.00	114.00	233.00	95.00	200.00	72.00	229.00	62.00	88.00
114	62.40	65.60	51.90	73.90	61.60	52.40	54.20	160.00	42.60	114.00	58.60*	43.60*
115	132.00*	223.00*	126.00	212.00	134.00*	236.00*	149.00*	267.00*	169.00*	262.00*	182.00	*
116	22.50	170.00	101.00	263.00	458.00*	208.00	122.00	24.30	25.00	79.20	70.00	118.00
117	48.40	79.10	64.90	130.20	104.40	63.50	66.70	46.80	66.70	96.80	99.60	181.20
118	130.00*	369.00*	246.00*	242.00	242.00*	353.00*	186.00*	359.00*	110.00	210.00	155.00	295.00

* = REJECTED

WATER LEGEND

1 - DISTILLED WATER
2 - TAP WATER
3 - SURFACE WATER
4 - WASTEWATER (C-44)
5 - WASTEWATER (C-45)
6 - WASTEWATER (C-46)

APPENDIX C (Continued)

TABLE C-2. RAW DATA FOR ISOPHORONE ANALYSIS BY WATER TYPE

	WATER 1		WATER 2		WATER 3		WATER 4		WATER 5		WATER 6	
HIGH YOUDEN PAIR	2	4	2	4	2	4	2	4	2	4	2	4
TRUE VALUE UG/L	475.00	400.00	475.00	400.00	475.00	400.00	475.00	400.00	475.00	400.00	475.00	400.00
LABORATORY NUMBER												
101	310.00	180.00	190.00	240.00	380.00	260.00	350.00	200.00	180.00	220.00	293.00	333.00
102	206.40	143.10	407.40	211.30	303.80	238.80	407.60	382.40	168.50	218.90	290.90	396.10
103	76.00*	0.00*	260.00	147.00	22.00*	14.00*	60.00*	36.00*	39.00	20.00	69.00	101.00
104	400.00	320.00	440.00	410.00	410.00	260.00	520.00	360.00	220.00	390.00	320.00	240.00
105	67.00	95.00	178.00	51.00	151.00	51.00	206.00*	123.00*	108.00	65.00	223.00	107.00
106	376.00	325.00	433.00	289.00	333.00	359.00	316.00	188.00	205.00	223.00	312.00	311.00
107	834.00*	545.00*	699.00	718.00	509.00*	685.00*	363.00	296.00	474.00	408.00	469.00	246.00
108	225.00*	67.90*	257.00	213.00	86.40*	147.00*	312.00*	47.10*	43.20*	63.80*	50.90	48.50
109	400.70	256.30	180.00	409.30	350.50	14.46*	332.00	356.00	473.10	411.00	412.70	400.90
110	196.00	175.00	269.00	162.00	269.00	162.00	328.00	188.00	276.00	216.00	342.00	167.00
111	81.00	136.00	43.00	200.00	150.00	124.00	192.00	185.00	188.00	98.00	172.00	138.00
112	67.88	181.40	333.40	*	356.80	280.60	284.20	297.00	311.90	270.10	330.10	256.10
113	477.00	356.00	471.00	509.00	562.00	491.00	591.00	454.00	800.00	388.00*	599.00	504.00
114	233.00	122.00	287.00	128.00	195.00	217.00	366.00	245.00	330.00	273.00	-36.40*	190.60*
115	539.00*	381.00*	386.00	*	406.00*	330.00*	*	499.00*	610.00*	522.00*	672.00	514.00
116	107.00	54.80	103.00	573.00	104.00	407.00	599.00	378.00	415.00	120.00	248.00	251.00
117	212.10	158.20	305.30	173.40	292.20	183.30	218.30	124.70	290.50	167.60	334.70	344.30
118	480.00*	370.00*	722.00	164.00	508.00*	451.00*	878.00*	405.00*	680.00	410.00	780.00	425.00

* = REJECTED

WATER LEGEND

1 - DISTILLED WATER
2 - TAP WATER
3 - SURFACE WATER
4 - WASTEWATER (C-44)
5 - WASTEWATER (C-45)
6 - WASTEWATER (C-46)

APPENDIX C (Continued)

TABLE C-3. RAW DATA FOR 2,4-DINITROTOLUENE ANALYSIS BY WATER TYPE

	WATER 1		WATER 2		WATER 3		WATER 4		WATER 5		WATER 6	
LOW YOUDEN PAIR	3	5	3	5	3	5	3	5	3	5	3	5
TRUE VALUE UG/L	1.40	1.00	1.40	1.00	1.40	1.00	1.40	1.00	1.40	1.00	1.40	1.00
LABORATORY NUMBER												
101	0.65	1.10	1.40	0.76	1.90	0.97	1.60	1.20	1.30	0.86	1.20	0.44
102	0.28*	0.48*	1.07	0.28	0.82	0.47	1.07	0.66	0.50	0.26	1.33	0.68
103	0.00*	0.00*	0.00*	0.00*	0.00*	0.00*	0.00*	0.00*	0.70*	0.40*	0.00*	0.80
104	0.93	0.58	1.30	0.79	0.81	0.68	1.10	0.67	0.83	0.66	1.00	0.65
105	0.90	0.60	0.80	0.70	0.60	0.20	0.80	0.60	0.80	0.60	1.10	0.40
106	0.90	0.81	1.62	0.64	1.68	0.60	1.68	0.70	1.36	0.10	1.44	1.04
107	1.69*	0.94*	1.27	0.51	1.30	0.70	1.68	1.01	1.12	0.75	1.51	1.35
108	1.95	1.08	2.20	0.89	2.01	1.18	0.78	0.59	0.91	0.61	0.47*	0.43*
109	1.33	0.72	1.56	0.76	0.60	0.83	1.19	0.68	1.68	1.05	1.06	0.77
110	1.01	0.96	1.46	0.87	0.95	0.59	0.57	0.40	1.11	0.61	1.13	0.67
111	0.61*	0.28*	1.68	0.56	0.74	0.38	1.04	0.84	0.83	0.67	0.97	0.65
112	1.14	0.84	1.53	*	0.94	1.38	1.17	0.83	2.77*	1.18*	*	1.12*
113	1.50	0.83	1.90*	1.10*	1.80*	0.87*	1.60	0.82	0.88	0.45	1.20	0.73
114	1.86	1.02	0.90	1.00	1.12	1.41	1.39	1.11	1.42	1.70*	0.95	0.86
115	*	0.92	1.53	0.60	0.97	0.11	0.63	1.43	0.41	0.29	1.24	0.61
116	1.27*	1.40*	2.73*	1.18*	2.11	0.98	4.20*	1.47*	2.66*	2.91*	3.96*	1.52*
117	0.56	0.52	0.76	0.53	0.34	0.22	0.83	0.82	0.36	0.24	0.52	0.30
118	1.70	1.70*	1.00	1.80*	1.80	2.00	1.20	0.90	*	1.00*	1.80	1.00

* = REJECTED

WATER LEGEND

1 - DISTILLED WATER
2 - TAP WATER
3 - SURFACE WATER
4 - WASTEWATER (C-44)
5 - WASTEWATER (C-45)
6 - WASTEWATER (C-46)

APPENDIX C (Continued)

TABLE C-3. RAW DATA FOR 2,4-DINITROTOLUENE ANALYSIS BY WATER TYPE

	WATER 1		WATER 2		WATER 3		WATER 4		WATER 5		WATER 6	
MEDIUM YOUDEN PAIR	1	6	1	6	1	6	1	6	1	6	1	6
TRUE VALUE UG/L	10.00	12.00	10.00	12.00	10.00	12.00	10.00	12.00	10.00	12.00	10.00	12.00
LABORATORY NUMBER												
101	8.00	11.00	6.30	8.70	6.50	6.80	5.40	9.90	9.00	8.70	7.90	6.40
102	2.25*	4.68*	*	*	3.36	6.49	5.31	8.49	5.96	5.13	5.83	6.77
103	2.80	5.70	3.40*	5.40*	0.00*	0.00*	2.10*	3.20*	3.00*	2.00*	4.40	4.80
104	5.00	7.70	3.70	6.10	5.70	9.50	4.90	6.90	5.70	7.50	7.30	6.50
105	6.20	6.80	6.80	3.60	5.10	7.30	5.00	5.20	4.30	7.70	4.90	8.20
106	8.41	10.00	3.75	10.00	3.05	5.50	8.41	8.53	7.24	9.46	7.24	6.31
107	11.20*	12.90*	11.40	12.60	9.57	12.10	7.71	9.12	7.58	9.20	8.88	10.30
108	8.59	4.91	8.12	10.50	7.27	9.79	5.37	3.96	2.61	6.11	3.56*	4.48*
109	8.13	8.61	7.71	8.84	5.17	9.13	6.93	8.18	9.59	11.93	7.82	8.72
110	5.10	4.51	5.00	6.54	3.19	4.30	2.64	3.66	4.46	6.00	4.19	5.30
111	2.42*	5.30*	3.82	3.00	4.20	6.91	6.00	5.25	4.20	6.05	3.90	7.85
112	8.70	10.58	8.49	10.17	8.16	10.56	6.59	*	9.37*	10.90*	9.62*	12.10*
113	13.00	12.00	11.00*	11.00*	10.00*	11.00*	8.60	10.00	6.50	9.30	9.00	7.40
114	6.20	5.68	5.84	5.96	5.94	5.79	5.23	7.47	6.55	7.12	6.51	6.61
115	9.53	9.70	8.52	9.58	8.65	9.20	9.57	9.59	5.68	5.84	8.40	*
116	14.20*	14.20*	19.40*	17.40*	23.90*	18.80*	13.00*	27.30*	19.00*	10.10*	14.10*	19.10*
117	3.81	4.18	5.15	6.50	4.07	4.00	5.99	4.70	5.64	5.27	6.42	2.94
118	9.20	8.20	9.90	6.00	8.30	8.30	9.10	5.00	9.90*	13.00*	9.40	16.00*

* = REJECTED

WATER LEGEND

1 - DISTILLED WATER
2 - TAP WATER
3 - SURFACE WATER
4 - WASTEWATER (C-44)
5 - WASTEWATER (C-45)
6 - WASTEWATER (C-46)

APPENDIX C (Continued)

TABLE C-3. RAW DATA FOR 2,4-DINITROTOLUENE ANALYSIS BY WATER TYPE

	WATER 1		WATER 2		WATER 3		WATER 4		WATER 5		WATER 6	
HIGH YOUDEN PAIR	2	4	2	4	2	4	2	4	2	4	2	4
TRUE VALUE UG/L	55.00	45.00	55.00	45.00	55.00	45.00	55.00	45.00	55.00	45.00	55.00	45.00
LABORATORY NUMBER												
101	52.00	32.00	35.00	39.00	47.00	32.00	52.00	32.00	31.00	30.00	42.00	28.00
102	18.20*	14.30*	39.10	16.50	30.90	26.10	39.03	33.70	27.40	28.20	32.80	33.70
103	22.10	24.30	23.30*	20.90*	4.00*	5.40*	8.40*	9.50*	8.80*	8.80*	11.50	30.10
104	36.00	42.00	42.00	40.00	32.00	29.00	48.00	25.00	25.00	37.00	42.00	23.00
105	14.60	20.70	24.20	32.50	29.20	19.60	40.10	37.30	20.50	22.70	26.90	20.30
106	43.20	31.20	45.00	31.50	37.10	33.90	38.60	29.10	21.10	4.61	36.20	31.50
107	53.30*	45.90*	55.00	46.10	45.00	38.60	40.40	36.00	44.20	36.50	43.50	32.20
108	19.60	16.10	18.70	17.50	17.30	16.60	33.80	14.60	11.80	12.80	13.40*	11.30*
109	34.17	27.68	18.99*	29.55	24.40	28.09	28.35	29.75	38.84	33.70	29.64	28.63
110	28.50	18.20	32.60	24.70	39.60	27.00	37.10	25.80	35.40	29.70	30.20	19.50
111	11.30*	13.90*	9.66	20.50	22.90	10.30	22.90	16.20	24.90	12.60	22.60	15.80
112	34.98	33.24	40.77	*	48.25	36.51	41.05	37.59	43.18*	36.95*	49.93*	43.42*
113	65.00	44.00	52.00*	50.00*	58.00*	49.00*	49.00	40.00	49.00	30.00*	53.00	47.00
114	39.70	17.00	40.70	18.40	27.20	16.60	41.60	23.80	40.30	29.90	27.30	25.30
115	49.90	35.70	44.80	*	39.20	9.80	*	45.00	41.10	33.70	66.40	41.30
116	45.90*	43.30*	35.70*	57.60*	11.60	56.00	67.60*	59.80*	67.60*	36.80*	73.20*	48.30*
117	21.38	16.25	36.18	14.06	21.10	18.07	36.12	21.56	31.75	19.76	39.37	29.02
118	31.00	38.00	31.00	32.00	26.00	40.00	22.00	26.00	39.00*	45.00*	44.00	25.00

* = REJECTED

WATER LEGEND

1 - DISTILLED WATER
2 - TAP WATER
3 - SURFACE WATER
4 - WASTEWATER (C-44)
5 - WASTEWATER (C-45)
6 - WASTEWATER (C-46)

APPENDIX C (Continued)

TABLE C-4. RAW DATA FOR 2,6-DINITROTOLUENE ANALYSIS BY WATER TYPE

	WATER 1		WATER 2		WATER 3		WATER 4		WATER 5		WATER 6	
LOW YOUDEN PAIR	3	5	3	5	3	5	3	5	3	5	3	5
TRUE VALUE UG/L	1.40	1.00	1.40	1.00	1.40	1.00	1.40	1.00	1.40	1.00	1.40	1.00
LABORATORY NUMBER												
101	0.64	0.92	1.10	0.73	1.50	0.91	1.30	1.20	1.30	0.71	0.81	0.29
102	0.21*	0.52*	1.03	0.32	0.93	0.68	1.08	0.62	0.82	0.37	1.05	0.67
103	0.40	0.40	0.50 <	0.40*<	0.40*	0.40*	0.40*	0.40*	0.60*	0.50*	0.40	0.70
104	0.89	0.65	1.00	0.79	0.71	0.69	0.84	0.61	0.72	0.73	0.91	0.65
105	1.00	0.70	1.10	0.80	0.90	0.60	1.10	0.80	1.10	0.70	1.40	0.70
106	0.80	0.88	0.57	0.28	1.74	0.93	1.48	0.89	1.25	0.06	1.44	1.00
107	1.52*	0.83*	1.13	0.55	1.18	0.69	1.29	0.91	1.10	0.97	1.34	1.16
108	1.48	0.90	1.52	0.65	1.37	0.92	0.59*	0.56*	0.68*	0.52*	0.32*	0.37*
109	1.36	0.93	1.47	0.95	0.60	1.00	1.26	0.94	1.77	1.57	1.13	1.05
110	0.99	1.11	1.32	0.91	0.58	0.42	0.49	0.49	0.80	0.54	1.01	0.68
111	0.71*	0.45*	1.74	0.81	1.02	1.02	1.46	1.06	0.73	0.55	0.78	0.80
112	0.76	0.75	1.22	*	0.92	0.91	0.94	0.87	1.20	0.82	*	1.17
113	1.20	0.77	1.40	1.00	1.20	0.71	1.30	0.79	1.20	0.80	0.98	0.85
114	1.81	1.33	0.82	1.11	1.10	1.69	1.05	1.12	1.19	1.26	0.80	0.76
115	*	1.00	1.26	0.75	1.17	0.68	0.94	1.25	1.34	0.71	1.31	0.91
116	0.93	1.50	2.57*	1.32*	2.01	1.70	4.17*	1.48*	2.16*	3.53*	2.49*	1.88*
117	0.53	0.62	0.94	0.64	0.33*	0.27*	0.78	0.61	0.29	0.22	0.43	0.34
118	1.60	2.40*	1.30	1.10	1.80	2.40*	1.00	2.80*	*	1.20	1.60	1.20

* = REJECTED

WATER LEGEND

1 - DISTILLED WATER
2 - TAP WATER
3 - SURFACE WATER
4 - WASTEWATER (C-44)
5 - WASTEWATER (C-45)
6 - WASTEWATER (C-46)

APPENDIX C (Continued)

TABLE C-4. RAW DATA FOR 2,6-DINITROTOLUENE ANALYSIS BY WATER TYPE

	WATER 1		WATER 2		WATER 3		WATER 4		WATER 5		WATER 6	
MEDIUM YOUDEN PAIR	1	6	1	6	1	6	1	6	1	6	1	6
TRUE VALUE UG/L	10.00	12.00	10.00	12.00	10.00	12.00	10.00	12.00	10.00	12.00	10.00	12.00
LABORATORY NUMBER												
101	7.20	10.00	5.60	9.60	5.80	7.60	4.90	9.40	7.60	8.30	7.20	6.60
102	2.75*	6.42*	*	*	3.34	7.29	6.06	9.37	7.26	7.86	6.59	8.31
103	2.90	6.50	3.70	6.70	0.00*	0.00*	2.10*	3.20*	3.80*	2.90*	4.50	6.10
104	5.70	8.30	4.10	5.10	6.70	8.60	5.30	7.30	7.30	9.40	7.40	7.10
105	7.20	8.90	7.40	5.80	7.40	8.80	6.10	7.00	6.50	9.00	6.20	10.00
106	8.93	11.10	4.52	12.50	3.42	5.26	8.37	9.04	8.09	9.92	7.66	7.06
107	11.60*	13.30*	12.40	14.10	10.50	12.40	7.84	9.45	10.00	12.70	10.10	10.60
108	5.11	3.77	4.89	5.14	4.44	4.92	4.13*	3.14*	2.18*	4.29*	3.48*	3.55*
109	8.72	10.09	8.77	9.13	5.81	10.66	8.06	9.50	10.81	12.16	8.46	10.01
110	5.98	5.17	5.89	7.93	4.66	4.73	3.14	5.15	5.00	7.20	5.17	6.17
111	3.75*	5.40*	4.35	6.52	5.25	8.90	6.25	6.92	4.37	6.97	4.31	9.13
112	7.84	10.24	8.06	10.22	7.27	10.38	6.23	*	7.84	8.85	8.86	11.47
113	11.00	9.60	11.00	13.00	8.10	10.00	7.80	9.60	6.80	9.20	7.60	7.40
114	7.06	5.71	5.98	6.19	5.77	6.78	4.69	6.01	6.07	7.25	6.23	5.92
115	9.04	9.98	9.12	9.98	9.00	10.70	10.70	11.90	9.36	10.60	9.55	*
116	13.20	15.70	15.10*	19.00*	26.80*	19.40*	23.00*	20.30*	14.80*	9.70*	13.80*	17.40*
117	3.97	4.58	5.34	5.57	4.29*	4.35*	5.85	4.09	5.09	5.87	6.60	2.61
118	9.30	10.00	8.10	14.00	9.60	11.00	10.00	12.00	9.80	14.00	12.00	13.00

* = REJECTED

WATER LEGEND

1 - DISTILLED WATER
2 - TAP WATER
3 - SURFACE WATER
4 - WASTEWATER (C-44)
5 - WASTEWATER (C-45)
6 - WASTEWATER (C-46)

APPENDIX C (Continued)

TABLE C-4. RAW DATA FOR 2,6-DINITROTOLUENE ANALYSIS BY WATER TYPE

	WATER 1		WATER 2		WATER 3		WATER 4		WATER 5		WATER 6	
HIGH YOUDEN PAIR	2	4	2	4	2	4	2	4	2	4	2	4
TRUE VALUE UG/L	60.00	50.00	60.00	50.00	60.00	50.00	60.00	50.00	60.00	50.00	60.00	50.00
LABORATORY NUMBER												
101	49.00	33.00	33.00	38.00	46.00	32.00	51.00	30.00	30.00	30.00	43.00	29.80
102	21.13*	18.14*	45.50	21.48	37.77	29.98	49.15	42.91	34.30	32.18	39.70	41.68
103	25.40	27.70	28.00	24.60	4.30*	5.60*	9.30*	9.50*	9.80*	9.90*	12.80	37.90
104	36.00	43.00	37.00	40.00	33.00	30.00	46.00	28.00	26.00	37.00	34.00	26.00
105	17.20	27.00	31.90	39.50	39.20	29.10	49.20	44.60	26.20	34.70	33.40	27.70
106	47.90	36.50	51.00	36.50	42.60	37.60	41.90	32.70	23.00	8.46	40.10	37.00
107	58.90*	51.30*	62.00	51.40	50.00	42.30	42.80	40.60	42.60	38.60	45.00	32.10
108	7.80	6.91	7.81	7.39	6.79	6.65	28.60*	6.07*	5.45*	5.60*	5.49*	5.05*
109	35.99	33.05	21.51*	32.49	27.83	29.58	32.50	33.40	41.69	37.50	33.40	32.61
110	33.50	26.60	36.60	34.00	45.10	33.20	43.00	32.80	35.40	35.40	35.20	26.10
111	16.20*	15.90*	16.00	25.70	31.80	13.20	28.00	19.70	32.90	15.90	28.10	20.20
112	32.60	34.78	44.18	*	50.12	39.10	42.36	39.58	42.70	38.03	57.56	44.46
113	60.00	41.00	49.00	50.00	51.00	43.00	45.00	37.00	52.00	30.00*	49.00	44.00
114	40.50	25.00	41.60	22.20	35.50	23.10	31.50	26.20	31.00	28.20	28.00	26.90
115	55.60	38.70	48.60	*	42.10	13.30	*	47.50	51.20	43.30	74.10	47.70
116	37.90	37.20	40.40*	63.90*	11.40	54.00	61.30*	60.60*	59.90*	30.10*	61.70*	52.30*
117	21.82	18.18	39.75	15.90	23.48*	20.87*	39.66	18.75	32.10	19.72	38.25	32.77
118	28.00	48.00	23.00	36.00	22.00	42.00	28.00	39.00	31.00	43.00	36.00	27.00

* = REJECTED

WATER LEGEND

1 - DISTILLED WATER
2 - TAP WATER
3 - SURFACE WATER
4 - WASTEWATER (C-44)
5 - WASTEWATER (C-45)
6 - WASTEWATER (C-46)

APPENDIX D

TABLE D-1. EFFECT OF WATER TYPE ON NITROBENZENE ANALYSIS

** POINT ESTIMATES **

DISTILLED WATER SLOPE:GAMMA(1) = .91628

WATER	INTERCEPT(WATER-DISTILLED)	SLOPE(WATER-DISTILLED)
2	-.3208	.0969
3	-.1829	.0609
4	-.2644	.0863
5	.0757	-.0071
6	-.3837	.1142

** ANALYSIS OF VARIANCE **

SOURCE	DF	SUM OF SQUARES	MEAN SQUARE	F	PROB
REG(DISTILLED)	1	660.61481	660.61481		
REG(WATER/DISTILLED)	10	3.73906	.17391	1.44	.1602
ERROR	490	127.38899	.25998		
TOTAL	501	791.74286			

** TABLE OF 95% CONFIDENCE INTERVALS FOR THE DIFFERENCES BETWEEN INTERCEPTS AND THE DIFFERENCES BETWEEN SLOPES **

WATER	INTERCEPT(WATER-DISTILLED) ESTIMATE	INTERCEPT(WATER-DISTILLED) INTERVAL	SLOPE(WATER-DISTILLED) ESTIMATE	SLOPE(WATER-DISTILLED) INTERVAL
2	-.3208	(-1.2582 , .6166)	.0969	(-.0874 , .2813)
3	-.1829	(-1.1472 , .7814)	.0609	(-.1285 , .2503)
4	-.2644	(-1.2223 , .6936)	.0863	(-.1022 , .2749)
5	.0757	(-.8791 , 1.0305)	-.0071	(-.1957 , .1815)
6	-.3837	(-1.3573 , .5898)	.1142	(-.0774 , .3058)

NOTE: IF ZERO IS CONTAINED WITHIN A GIVEN CONFIDENCE INTERVAL THEN THERE IS NO STATISTICAL SIGNIFICANCE BETWEEN DISTILLED WATER AND THE CORRESPONDING WASTEWATER FOR THE ASSOCIATED PARAMETER(INTERCEPT/SLOPE).

THE SLOPE AND INTERCEPT ESTIMATES FROM THIS ANALYSIS ARE NOT THE SAME AS THOSE OBTAINED FROM THE PRECISION AND ACCURACY REGRESSIONS PERFORMED EARLIER.

APPENDIX D (Continued)

TABLE D-2. EFFECT OF WATER TYPE ON ISOPHORONE ANALYSIS

** POINT ESTIMATES **

DISTILLED WATER SLOPE:GAMMA(1) = .92473

WATER	INTERCEPT(WATER-DISTILLED)	SLOPE(WATER-DISTILLED)
2	-.1367	.0716
3	-.3498	.0954
4	-.6091	.1570
5	.0648	.0177
6	.1858	.0216

** ANALYSIS OF VARIANCE **

SOURCE	DF	SUM OF SQUARES	MEAN SQUARE	F	PROB
REG(DISTILLED)	1	629.72773	629.72773		
REG(WATER/DISTILLED)	10	5.38208	.53821	1.70	.0789
ERROR	488	154.92894	.31748		
TOTAL	499	790.03875			

** TABLE OF 95% CONFIDENCE INTERVALS FOR THE DIFFERENCES BETWEEN INTERCEPTS AND THE DIFFERENCES BETWEEN SLOPES **

WATER	INTERCEPT(WATER-DISTILLED) ESTIMATE	INTERVAL	SLOPE(WATER-DISTILLED) ESTIMATE	INTERVAL
2	-.1367	(-1.1995 , .9261)	.0716	(-.1406 , .2838)
3	-.3498	(-1.4716 , .7720)	.0954	(-.1296 , .3203)
4	-.6091	(-1.7395 , .5213)	.1570	(-.0691 , .3832)
5	.0648	(-1.0081 , 1.1378)	.0177	(-.1973 , .2327)
6	.1858	(-.9108 , 1.2825)	.0216	(-.1958 , .2389)

NOTE: IF ZERO IS CONTAINED WITHIN A GIVEN CONFIDENCE INTERVAL THEN THERE IS NO STATISTICAL SIGNIFICANCE BETWEEN DISTILLED WATER AND THE CORRESPONDING WASTEWATER FOR THE ASSOCIATED PARAMETER(INTERCEPT/SLOPE).

THE SLOPE AND INTERCEPT ESTIMATES FROM THIS ANALYSIS ARE NOT THE SAME AS THOSE OBTAINED FROM THE PRECISION AND ACCURACY REGRESSIONS PERFORMED EARLIER.

APPENDIX D (Continued)

TABLE D-3. EFFECT OF WATER TYPE ON 2,4-DINITROTOLUENE ANALYSIS

** POINT ESTIMATES **

DISTILLED WATER SLOPE:GAMMA(1) = .92259

WATER	INTERCEPT(WATER-DISTILLED)	SLOPE(WATER-DISTILLED)
2	-.0142	.0011
3	-.1679	.0185
4	-.0648	.0213
5	-.3372	.0739
6	-.0800	.0295

** ANALYSIS OF VARIANCE **

SOURCE	DF	SUM OF SQUARES	MEAN SQUARE	F	PROB
REG(DISTILLED)	1	1100.35664	1100.35664		
REG(WATER/DISTILLED)	10	2.98495	.29850	2.48	.0066
ERROR	491	59.07183	.12031		
TOTAL	502	1162.41342			

** TABLE OF 95% CONFIDENCE INTERVALS FOR THE DIFFERENCES BETWEEN INTERCEPTS AND THE DIFFERENCES BETWEEN SLOPES **

WATER	INTERCEPT(WATER-DISTILLED) ESTIMATE	INTERVAL	SLOPE(WATER-DISTILLED) ESTIMATE	INTERVAL
2	-.0142	(-.2843 , .2559)	.0011	(-.0995 , .1017)
3	-.1679	(-.4309 , .0950)	.0185	(-.0785 , .1156)
4	-.0648	(-.3262 , .1965)	.0213	(-.0762 , .1187)
5	-.3372	(-.6094 , -.0650)	.0739	(-.0271 , .1750)
6	-.0800	(-.3479 , .1879)	.0295	(-.0692 , .1282)

NOTE: IF ZERO IS CONTAINED WITHIN A GIVEN CONFIDENCE INTERVAL THEN THERE IS NO STATISTICAL SIGNIFICANCE BETWEEN DISTILLED WATER AND THE CORRESPONDING WASTEWATER FOR THE ASSOCIATED PARAMETER(INTERCEPT/SLOPE).

THE SLOPE AND INTERCEPT ESTIMATES FROM THIS ANALYSIS ARE NOT THE SAME AS THOSE OBTAINED FROM THE PRECISION AND ACCURACY REGRESSIONS PERFORMED EARLIER.

APPENDIX D (Continued)

TABLE D-4. EFFECT OF WATER TYPE ON 2,6-DINITROTOLUENE ANALYSIS

** POINT ESTIMATES **

DISTILLED WATER SLOPE:GAMMA(1) = .91451

WATER	INTERCEPT(WATER-DISTILLED)	SLOPE(WATER-DISTILLED)
2	-.0542	.0250
3	-.0188	-.0204
4	-.0772	.0362
5	-.2060	.0624
6	-.1138	.0486

** ANALYSIS OF VARIANCE **

SOURCE	DF	SUM OF SQUARES	MEAN SQUARE	F	PROB
REG(DISTILLED)	1	1190.87612	1190.87612		
REG(WATER/DISTILLED)	10	1.58691	.15869	1.47	.1470
ERROR	516	55.69779	.10794		
TOTAL	527	1248.16082			

** TABLE OF 95% CONFIDENCE INTERVALS FOR THE DIFFERENCES BETWEEN INTERCEPTS AND THE DIFFERENCES BETWEEN SLOPES **

WATER	INTERCEPT(WATER-DISTILLED) ESTIMATE	INTERVAL	SLOPE(WATER-DISTILLED) ESTIMATE	INTERVAL
2	-.0542	(-.2920 , .1835)	.0250	(-.0622 , .1123)
3	-.0188	(-.2581 , .2205)	-.0204	(-.1076 , .0668)
4	-.0772	(-.3215 , .1671)	.0362	(-.0528 , .1252)
5	-.2060	(-.4498 , .0377)	.0624	(-.0263 , .1512)
6	-.1138	(-.3532 , .1256)	.0486	(-.0385 , .1357)

NOTE: IF ZERO IS CONTAINED WITHIN A GIVEN CONFIDENCE INTERVAL THEN THERE IS NO STATISTICAL SIGNIFICANCE BETWEEN DISTILLED WATER AND THE CORRESPONDING WASTEWATER FOR THE ASSOCIATED PARAMETER(INTERCEPT/SLOPE).

THE SLOPE AND INTERCEPT ESTIMATES FROM THIS ANALYSIS ARE NOT THE SAME AS THOSE OBTAINED FROM THE PRECISION AND ACCURACY REGRESSIONS PERFORMED EARLIER.